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A Spectrophotometric Investigation of the System Iron (III) Perchlorate-Ethylene Glycol-Water

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A SPECTROPHOTOMETRIC INVESTIGATION OF THE SYSTEM IRON(III) PERCHLORATE-ETHYLENE GLYCOL-WATER

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This thesis is approved as a creditable, independent investigation by a candidate for the degree, Master of Science, and acceptable as meeting the thesis requirements for this degree; but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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G. H. A.

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INTRODUCTION

The need for a more complete quantitative description of aqueous electrolytic solutions has led to a renewal, in recent years, of interest in determining the stability constants and formulas for the species present in these solutions. These studies have indicated that the species present are not as simple as previously believed. Of particular interest are the species formed by the interaction of polyvalent metal ions with the solvent molecules and with the anions present.

It was felt that an investigation of a polyvalent metal ion in a mixed solvent could be of value in helping to clarify the interaction of metal ions with the solvent. This investigation was planned as a preliminary study of the system iron(III) perchlorate–ethylene glycol–water, the major portion of the data to be obtained spectrophotometrically.

SURVEY OF THE LITERATURE

Studies of the stepwise formation of complexes first appeared in the early nineteen hundreds, but after a brief period of activity, very little was published until the nineteen thirties. At this time some information was published by A. W. Thomas and coworkers (61, 62) of Columbia University. He apparently was the first American chemist to interpret the data of aqueous chemistry in terms of concepts proposed by Werner. In the years following there has been an increasing amount of material published on ionic equilibria and complex ions.

Experimental Techniques and Evaluation of Data

Numerous experimental techniques (38) could be proposed for detecting complex ions, and many different methods have been developed. Any technique measuring a physical or chemical property altered by the formation of covalent ions or compounds by metal ions could help demonstrate the presence and constitution of coordination compounds or complex ions. While the evaluation of data from a single technique may not offer sufficient information, a combination of data from some of these techniques may give definite evidence for complex formation. Of all possible techniques, three seem to be the most commonly used: e.m.f. measurements, polarographic measurements and spectrophotometric measurements.

Perhaps the best method for the determination of the species present in solution is the e.m.f. method. This method allows the determination of the central ion and the ligand concentration with good

accuracy. A complete discussion of experimental techniques and the treatment of data for this method is available in a series of more than twenty papers originating from methods proposed by Biedermann, Hietanen, and Sillén (7, 25, 56, 57, 58). A summary of the results of this comprehensive study has recently been published (8, 9).

The polarographic method can be used to determine equilibrium constants for complex ions. In this method it must be determined that the reduction of the metal ion and the complex ion with that metal in the same oxidation state, is reversible and involves the same number of electrons. The determination of the equilibrium constant, if the above is true, becomes simply the combination of the half-wave potentials.

The spectrophotometric method, used in this study, differs from the e.m.f. method in that instead of determining the concentration of individual species, a function of the concentration (the absorbancy), is measured. The value of this function may be due to a summation of contributions from more than one species absorbing at that particular wave length. Since absorbancy is proportional to concentration there are N proportionality constants of unknown value for N species contributing to the absorbancy. In addition to the unknown equilibrium constants we now have N more unknowns.

Until recently, no method has been available for easily evaluating data obtained spectrophotometrically when three or more species are present. A recent paper (52) has reviewed the methods used to evaluate spectrophotometric data. The authors have developed a new method which allows simultaneous determination of the stability constant and formula

of a complex under conditions where three or more species are present.

Mixed Solvent Systems

Studies of metal ions in mixed solvent systems follow the same general historical trend as aqueous ionic equilibria work. There was some activity in the early nineteen hundreds and a lapse of interest until the nineteen forties. Part of the early work was done by Jones and coworkers (29, 30, 31). From their study of the absorption spectra of metal ions in mixed solvents, generally alcohols and water, they concluded that the deviation from Beer's law, observed in these solvents, is the rule rather than the exception. These deviations were ascribed to the formation of solvates. Merton (41) concluded the same thing from his studies in various solvents.

In 1943, Garrett et al. (19) published a paper on the system lead chloride-ethylene glycol-water. Using solubility and cell data, the stability of the solvate present was reported.

Spectrophotometric studies, in recent years, have been made by Baldwin and Sverbely (3), Minc and Libus (43), Cohen et al. (18) and Glikman et al. (20).

The study made by Baldwin and Sverbely was of iron(III) thiocyanate solutions in various solvent pairs. A shift of the maximum toward shorter wave lengths was observed as the percentage of water is increased. They explained this in terms of an equilibrium between two species of thiocyanate complexes of different intensities of absorption.

Minc and Libus observed, in their study of copper(II) nitrate in

water-ethanol mixtures, that two maxima were present in solutions containing ethanol. They attribute these maxima to differences in chemical solvation of copper(II) ion by ethanol.

Cohen et al. studied kinetically the reaction,

$$Np(IV) + Np(VI) \longrightarrow 2Np(V)$$

in a medium to ethylene glycol-perchloric acid-water by following the increase in absorption of Np(V) ion at 983 millimicrons. They reported, however, that the ethylene glycol became involved in the reaction.

The study, by Glikman et al. of iron(III) perchlorate in ethanol-water, was made to explain the photochemical reduction of iron(III) ion to iron(II) ion in the presence of ethanol. An absorption maximum at 320 millimicrons, in solutions containing ethanol, was shifted to the longer wave lengths as the percentage of ethanol was increased.

Lerner et al. (36) have published a review concerning the interaction of iron compounds with solvent systems.

Iron(III) Ion Systems

In addition to those systems mentioned previously which deal with iron(III) ion, there has been a considerable amount of work published concerning the hydrolysis of iron(III) ion.

Miscellaneous Studies

Apparently the first person to calculate a hydrolysis constant for iron(III) hydrolysis was Bjerrum (10). He calculated the first hydrolysis constant from data obtained from a conductimetric study of

iron(III) ion.

Jander (27, 28) made a study of iron(III) ion hydrolysis using the diffusion coefficient of iron(III) perchlorate solutions. He postulated several species of hydrolysis products for a normal perchloric acid medium, some of these products occurring as the result of oxalation and olation reactions.

Aumeras and Mounic (2) published a study of the hydrolysis of iron(III) chloride solutions using "coefficients of magnetization".

Studies Using the e.m.f. Method

Linstrand (37), Bray and Hersey (12) and Brosset (13) calculated the first hydrolysis constant for iron(III) hydrolysis from e.m.f. data. Hedström (24), noting the disagreement among the previous authors, studied the hydrolysis of iron(III) perchlorate in a constant ionic medium (3.0 molar perchlorate).

Spectrophotometric Studies

Quite a number of papers based on absorption spectra are available.

Cathala and Cluzel (14, 15, 16, 17) used iron(III) nitrate solutions to study the hydrolysis of iron(III) ion. They studied the system at constant concentration and varying pH, concluding that the development of color was not due to formation of small amounts of iron(III) hydroxide, as was generally thought, but to intermediate products. Their study of buffered solutions showed that the speed of aging was dependent on the iron(III) concentration, and that there was a "threshold" value for given concentrations of iron(III) ion above which the absorption of a solution

was independent of pH.

Kiss et al. (33) studied iron(III) perchlorate solutions in 2.55 molar perchloric acid, concluding that they had determined a standard curve for hydrated iron(III) ion. Later authors do not agree with his conclusion. In a subsequent paper, Kiss and Sandorty (32) bring together many of the previous absorption spectra of metal perchlorates, including iron, for comparison.

The prototype paper for this system is considered to be Rabinowitch and Stockmayer's (51) study of the iron(III) perchlorate absorption spectra. They separated the hydrated iron(III) ion spectra from the spectra of the first hydrolysis product, $\left[Fe(OH)\right]^{+2}$, by a study at different ionic strengths, temperatures, and by addition of hydroxyl ion. They reported a heavy double peak absorption band at 200 to 240 millimicrons and three much weaker bands in the visible range. One of these, at 407 millimicrons, was of particular interest because it was sharp (half-width 20 millimicrons). The other two were more diffuse, a band at 550 millimicrons with a half-width of 135 millimicrons. They state that previous workers missed the peak at 407 millimicrons because of insufficient acidity, although Kiss, Ábraham and Hegedus (33) reported a pH less than zero using a 2.55 molar perchloric acid medium. In addition, Rabinowitch and Stockmayer reported no apparent complexing with perchlorate ions.

Olson and Simonson (47, 48) published the results of their study on the hydrolysis of iron(III) ion in 1949. They were interested in the effect of addition of salts to aqueous solutions of iron(III) ion. They added sodium perchlorate and lanthanum perchlorate, these substances

producing identical shifts of equilibrium for identical normalities. However in solutions of the same ionic strength, the addition of sodium perchlorate produced a much greater change than did the addition of lanthanum perchlorate. They conclude, that if this is true, there should be a restudy of Debye-Hückel's approach to the calculation of activity coefficients of ions. They also report from their spectrophotometric study that the equilibrium is dependent upon the perchlorate ion concentration.

Siddal and Vosburgh (55) made a study of solutions containing iron(III) ion in which they developed a method of calculating the first hydrolysis constant for mononuclear species. Later, Milburn and Vosburgh (42) published a paper on calculation of hydrolysis constants for polynuclear species. The latter paper is in disagreement with Rabinowitch and Stockmayer concerning the equation developed for calculating hydrolysis constants.

Papers by Mulay and Selwood (44, 45) present a comparison of spectrophotometric and magnetic susceptibility data. They used solutions of varying pH which were 0.04 molar in iron(III) perchlorate with an ionic strength of three (mostly sodium perchlorate). They explain their results by assuming the absorption at 240 millimicrons results from hydrated iron(III) ion and $\left[Fe(OH)\right]^{+2}$, the absorption at 335 millimicrons is due to dimers, the dimer $\left[Fe_2(OH)_2\right]^{+4}$ is diamagnetic, and the molar absorbancy indices of $\left[Fe(OH)\right]^{+2}$ is greater than that of iron(III) ion at 240 millimicrons.

Some Polyvalent Metal Complexes

It is interesting to note at this point some results reported by Milburn and Vosburgh (42) and Sutton (59). They reported indications of a perchlorate complex at high perchlorate ion concentrations. Milburn and Vosburgh obtained this indication at an ionic strength of 2.8 with 0.05 molar iron(III) perchlorate solutions. Sutton reported these same results in solutions above an ionic strength of one.

Some interesting work has been done on iron(III) ion complexing with polyhydroxy alcohols by Traube and coworkers (63, 64, 65, 66, 67). Indications that the complex was important in the oxidation of the alcohol were mentioned.

An absorption study of a glucoric acid-iron(III) ion complex was published by Tanabe and coworkers (60). They reported the decomposition of this complex by light.

Grun and coworkers (22, 23), although not working with iron, showed that ethylene glycol formed stable coordination compounds with nickel, copper, cobalt, and chromium.

Oda et al. (46) studied the effect of copper(III) ion on the photochemical oxidation of alcohols.

Photoreduction of Iron(III) Ion

Several possible mechanisms have been proposed for the photoreduction of aqueous iron(III) ion. Some of these are concerned with photoreduction of iron(III) ion in the presence of oxidizable "impurities" (5, 20, 54), while others deal with the reduction in water alone (20, 21).

Bates and Uri (5) report that benzyl alcohol is oxidized to benzaldehyde by a photo-initiated reaction involving iron(III) ion. They propose a mechanism which involves the formation of a free hydroxyl radical which attacks the organic material present forming an organic free radical. The organic free radical is then oxidized by iron(III) ion.

Saldick and Allan (54) propose an alternate mechanism involving formation of an organic free radical by reaction with the excited complex $Fe^{+2}OH$ and subsequent oxidation of this free radical by iron(III) ion. They, however, conclude that their data fits the Bates and Uri mechanism better.

Good and Purdon (21) report that a study of iron(III) ions in aqueous solution indicates that the reduction of iron(III) ion is possible in water alone. They also report a secondary, dark hydrolytic reaction.

Glikman et al. (20) in their study of the photoreduction of iron (III) ion in ethanol, note that in aqueous solution, the electron transfer occurs in a hydrated ion envelope; while in cases where ethanol is present, the situation is one involving a bonding of the iron(III) ion and ethanol. The latter case makes the electron transfer much simpler because of the complexity of the bound molecule.

Reference Books

Several good reference books (4, 38, 39, 40), dealing with complexes and/or spectrophotometry, are available. Those most often used are included here.

EXPERIMENTAL DETAIL

Reagents and Apparatus

The study was made with distilled water having a specific conductance of less than 10^{-6} mhos. Reagent grade non-yellow iron(III) perchlorate was obtained from G. Frederick Smith Chemical Company, as was reagent grade anhydrous sodium perchlorate. The ethylene glycol was a Fisher certified reagent. The perchloric acid was a Baker analyzed reagent.

The major portion of the work was done on a Beckman model DU quartz spectrophotometer. The cells used were matched silica cells with a length of approximately one centimeter. In some cases silica cell spacers were used to decrease the cell length to approximately one millimeter. The temperature of the cell compartment was maintained at 25.00 ± 0.05 degrees centigrade by use of a thermospacer attachment and a constant temperature bath.

Preparation of Solutions

A stock solution of iron(III) perchlorate was prepared and analyzed for iron(III) and hydrogen ion.

The solutions to be studied were prepared by dilution. The first dilutions, to approximately 10^{-2} molar iron(III) perchlorate, were made from the stock solution. The next dilutions to 10^{-3} molar were made from the 10^{-2} molar solutions. The dilutions to 10^{-4} molar were made from the 10^{-3} molar solutions.

Several analytical methods for the analysis of total iron were considered. The dichromate method was chosen after a preliminary analysis on standard iron wire dissolved in hot concentrated perchloric acid showed it to be accurate within two parts per thousand.

There was one variation from the standard method used for iron(III) chloride. Just prior to the reduction of iron(III) ion, 10 milliliters of concentrated hydrochloric acid were added to the sample. This was done to speed up the reduction of iron(III) ion since it is slow in the absence of chloride ion when stannous chloride is used as the reducing agent (48).

The stock solution was found to be 0.1038 molar iron(III) perchlorate. The stock solution was also analyzed for an excess of perchloric acid. Three methods were used for the analysis. In the first method, a sample of the stock solution was titrated directly with standard sodium hydroxide to a phenolphthalein end point. The iron(III) hydroxide formed was allowed to settle before addition of more sodium hydroxide so that the end point could be observed more clearly. In the second method, the same type of titration was carried out with a pH meter. In the third method, a sample was washed through an ion exchange resin in the hydrogen form, and the resulting solution titrated with sodium hydroxide. A correction was made in all three methods for the hydroxide ion which was or would have been used in reacting with iron(III) ion. There was good agreement in the three methods with the concentration of perchloric acid being determined as 8.43×10^{-2} molar.

To facilitate the preparation of the dilute iron(III) perchlorate solutions, which were to contain ethylene glycol, stock solvent mixtures

of 15, 35, 55, 75 and 90 percent ethylene glycol, were prepared. These were used in diluting the solutions to volume.

There is a volume change in mixing ethylene glycol and water (53); so the solvent was made up by weight percent. The stock solvent mixtures were prepared by mixing calculated volumes of water and ethylene glycol. These volumes were calculated using the densities of ethylene glycol and water at 25 degrees centigrade as 1.1133 and 0.99707 grams per milliliter, respectively.

In preparing the eighteen iron(III) perchlorate solutions to be used, plus the corresponding blanks for each solution, thirty 100-milliliter volumetric flasks were calibrated. Into 18 of these were placed a number of grams of anhydrous sodium perchlorate, iron(III) perchlorate solution and where necessary additional amounts of perchloric acid and ethylene glycol. These were then diluted to volume with the correct solvent or solvent mixture. The remaining 12 flasks were used for preparation of blanks.

Preparation of $1.03\frac{1}{2} \times 10^{-2}$ Molar Solutions

The $1.03\frac{1}{2} \times 10^{-2}$ molar iron(III) perchlorate solutions were prepared as follows. Into each of six 100-milliliter volumetric flasks was placed 12.25 grams of solid sodium perchlorate. This was the amount necessary to adjust the ionic strength of the final solution to 1.07. A 9.96 milliliter sample of the 0.1038 molar stock solution was then added to each flask. This made it necessary to compensate, in those solutions which were to contain definite percentages of ethylene glycol, for the water introduced by adding an aqueous stock solution. The addi-

tional amount of ethylene glycol necessary was calculated from the density and concentration of the stock solution. The density of the stock solution was determined as 1.0283 grams per milliliter. After adding this amount of ethylene glycol the solution was diluted to volume with the correct solvent or solvent mixture.

Preparation of 1.030×10^{-3} Molar Solutions

The 1.030×10^{-3} molar iron(III) perchlorate solutions were prepared as follows. Into each of six 100-milliliter volumetric flasks was placed 11.7 grams of sodium perchlorate. This was the amount necessary to adjust the ionic strength to 1.07. A 9.96 milliliter sample of iron(III) perchlorate solution, taken from the corresponding 1.034×10^{-2} molar solutions already prepared, was placed in each flask. In addition, since the 1.034×10^{-2} iron(III) perchlorate solutions contained an excess of perchloric acid, a volume of 0.238 molar perchloric acid was added to the 1.030×10^{-3} molar iron(III) perchlorate solutions in order that the molar concentration of perchloric acid would be constant. The addition of aqueous perchloric acid made it again necessary to compensate for introduced water by adding ethylene glycol. The amount to be added was calculated in a manner similiar to that used previously. The density of the 0.238 molar perchloric acid was determined to be 1.0098 grams per milliliter. From this value and the concentration the amount of water added was calculated. The amount of ethylene glycol necessary was added, and the solutions then diluted to volume with the correct solvent or solvent mixture.

Preparation of 1.026×10^{-4} Molar Solutions

The 1.026×10^{-4} molar iron(III) perchlorate solutions were prepared in exactly the same manner as the 1.030×10^{-3} molar iron(III) perchlorate solutions. The iron(III) perchlorate sample was obtained from the corresponding 1.030×10^{-3} molar iron(III) perchlorate solutions.

Blanks

Twelve blank solutions were prepared. Six of these were used with the 1.034×10^{-2} molar solutions and the other six with either the 1.030×10^{-3} molar or 1.026×10^{-4} molar iron(III) perchlorate solutions, since these contained the same concentration of everything but iron(III) perchlorate.

Technique

The cells were readied for use by washing in glass cleaning solution, rinsing in distilled water and drying with paper tissue and cotton tipped sticks. They were then rinsed three or four times with the solution that they were to contain and then filled.

When a cell spacer was used it was inserted so as to be oriented in its cell the same way each time. The cells, themselves, were placed in the same position in the cell holder each time.

In operating the spectrophotometer the controls were always rotated so that the final settings were the result of a clockwise motion of the scale. This was done to eliminate any error from mechanical play in the control mechanism.

The hydrogen bulb was used as a light source for all readings of 320 millimicrons and below and the tungsten bulb for 320 millimicrons and above. A filter was used between 320 and 400 millimicrons.

The first technique used in obtaining an absorption spectrum was to obtain that portion of the spectrum below 320 millimicrons. After this portion was obtained for all eighteen solutions the portion 320 millimicrons and above was obtained. This method was abandoned in favor of obtaining the complete spectrum of each solution in one operation.

EXPLANATION OF TABLES AND FIGURES

The symbols used in this study are those recommended by the National Bureau of Standards for spectrophotometric data and include the following: λ = wave length, mμ = millimicron, b = cell length, A_s = absorbancy, A'_s = corrected absorbancy, and a_M = molar absorbancy index.

The cell corrections are given in absorbancy units and the slit width in millimeters.

The curves (Figures 4, 5, 6) numbered 1, 2, 3, 4, 5 and 6 correspond to solutions containing zero, 15, 35, 55, 75 and 90 percent ethylene glycol by weight. The circles on the left side are an estimate of the spectrophotometric accuracy in that region. They apply to the ordinate only and correspond to a plus or minus one percent of the absorbancy reading.

In figures 2 and 3, the values plotted were taken from the maxima occurring in the long wave region for those solutions that showed a maximum. For those solutions which did not have a maximum in the long wave region, generally those without or with a low percent of ethylene glycol, the values plotted are those at 330 millimicrons.

DATA

TABLE I. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
250	1/18/59	0.5	2.68	-0.003	2.68	2670
260		0.5	2.53	+0.001	2.53	2520
270		0.5	1.850	+0.002	1.848	1840
280		0.5	1.201	+0.001	1.200	1200
290		0.5	0.750	+0.001	0.749	750
300		0.5	0.540	0.000	0.540	540
310		0.5	0.485	+0.001	0.484	480
320		0.5	0.516	+0.001	0.515	510
320		0.3	0.516	0.000	0.516	510
330		0.3	0.538	0.000	0.538	540
340		0.3	0.499	0.000	0.499	500
350		0.3	0.379	0.000	0.379	380
360		0.3	0.241	-0.001	0.242	240
370		0.15	0.134	-0.001	0.135	140
380		0.15	0.069	-0.001	0.070	70
390		0.15	0.036	-0.001	0.037	40
400		0.15	0.020	-0.001	0.021	20

TABLE II. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 15 PERCENT ETHYLENE GLYCOL-85 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
230	1/19/59	0.5	2.95	+0.025	2.92	2910
240		0.5	2.95	-0.003	2.95	2940
250		0.5	2.80	-0.001	2.80	2790
260		0.5	2.59	+0.003	2.59	2580
270		0.5	1.92	+0.003	1.92	1910
280		0.5	1.222	+0.003	1.219	1210
290		0.5	0.785	+0.002	0.783	780
300		0.5	0.589	+0.002	0.587	590
310		0.5	0.549	+0.002	0.547	550
320		0.5	0.594	+0.001	0.593	590
320	1/26/59	0.5	0.597	0.000	0.597	590
330		0.5	0.652	0.000	0.652	650
340		0.2	0.639	0.000	0.639	640
350		0.2	0.538	0.000	0.538	540
360		0.2	0.408	0.000	0.408	410
370		0.2	0.292	0.000	0.292	290
380		0.2	0.212	0.000	0.212	210
390		0.2	0.160	0.000	0.160	160
400		0.05	0.122	0.000	0.122	120

TABLE III. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 35 PERCENT ETHYLENE GLYCOL-65 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
250	1/19/59	0.5	2.91	-0.007	2.92	2910
260		0.5	2.63	-0.004	2.63	2620
270		0.5	1.955	-0.002	1.957	1950
280		0.5	1.305	-0.002	1.307	1300
290		0.5	0.895	-0.002	0.897	890
300		0.5	0.730	-0.002	0.732	730
310		0.5	0.715	-0.002	0.717	720
320		0.5	0.798	-0.002	0.800	800
320	1/27/59	0.5	0.741	+0.002	0.739	740
330		0.5	0.819	+0.002	0.817	810
340		0.2	0.835	+0.002	0.833	830
350		0.2	0.756	+0.001	0.755	750
360		0.2	0.632	+0.001	0.631	630
370		0.2	0.516	+0.001	0.515	510
380		0.2	0.420	+0.001	0.419	420
390		0.2	0.340	+0.001	0.339	340
400		0.05	0.271	+0.001	0.270	270

TABLE IV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 55 PERCENT ETHYLENE GLYCOL-45 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
240	1/19/59	0.5	2.63	-0.006	2.64	2630
250		0.5	2.82	-0.003	2.82	2810
260		0.5	2.79	0.000	2.79	2780
270		0.5	2.10	+0.001	2.10	2090
280		0.5	1.462	0.000	1.462	1460
290		0.5	1.090	0.000	1.090	1090
300		0.5	0.939	0.000	0.939	940
310		0.5	0.982	0.000	0.982	980
320		0.5	1.142	0.000	1.142	1140
320	1/26/59	0.5	1.103	+0.002	1.101	1100
330		0.5	1.252	+0.002	1.250	1250
340		0.2	1.313	+0.002	1.311	1310
350		0.2	1.257	+0.002	1.255	1250
360		0.2	1.133	+0.002	1.131	1130
370		0.2	0.970	+0.002	0.968	960
380		0.2	0.825	+0.002	0.823	820
390		0.2	0.692	+0.002	0.690	690
400		0.05	0.567	+0.001	0.575	570

TABLE V. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 75 PERCENT ETHYLENE GLYCOL-25 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
270	1/20/59	0.5	2.29	+0.001	2.29	2280
280		0.5	1.668	+0.001	1.667	1660
290		0.5	1.298	0.000	1.298	1290
300		0.5	1.188	+0.001	1.187	1180
310		0.5	1.279	+0.001	1.278	1270
320		0.5	1.494	0.000	1.494	1490
320	1/27/59	0.5	1.47	0.000	1.47	1460
330		0.5	1.68	0.000	1.68	1670
340		0.2	1.795	0.000	1.795	1790
350		0.2	1.750	0.000	1.750	1740
360		0.2	1.635	0.000	1.635	1630
370		0.2	1.452	0.000	1.452	1450
380		0.2	1.254	0.000	1.254	1250
390		0.2	1.067	0.000	1.067	1060
400		0.05	0.870	0.000	0.870	870

TABLE VI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 90 PERCENT ETHYLENE GLYCOL-10 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
270	1/19/59	0.5	2.42	+0.002	2.42	2410
280		0.5	1.90	+0.002	1.90	1890
290		0.5	1.543	+0.003	1.540	1530
300		0.5	1.442	+0.003	1.439	1430
310		0.5	1.582	+0.003	1.579	1570
320		0.5	—	—	—	—
320	1/27/59	0.5	1.835	0.000	1.835	1830
330		0.5	2.17	0.000	2.17	2160
340		0.2	2.37	0.000	2.37	2360
350		0.2	2.41	0.000	2.41	2400
360		0.2	2.24	0.000	2.24	2230
370		0.2	2.02	0.000	2.02	2010
380		0.2	1.76	0.000	1.76	1750
390		0.2	1.50	0.000	1.50	1500
400		0.05	1.234	0.000	1.234	1230

TABLE VII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/18/59	0.5	0.487	+0.116	0.371	3710
230		0.5	0.419	+0.023	0.396	3960
240		0.5	0.395	-0.006	0.401	4010
250		0.5	0.355	-0.004	0.359	3590
260		0.5	0.274	+0.001	0.273	2730
270		0.5	0.182	+0.002	0.180	1800
280		0.5	0.112	+0.002	0.110	1100
290		0.5	0.070	+0.001	0.069	691
300		0.5	0.049	+0.001	0.048	480
310		0.5	0.039	+0.001	0.038	380
320		0.5	0.029	+0.001	0.028	280
320	1/25/59	0.5	0.027	+0.002	0.025	250
330		0.5	0.023	+0.002	0.021	210
340		0.2	0.017	+0.002	0.015	150
350		0.2	0.012	+0.002	0.010	110
360		0.2	0.007	+0.002	0.005	50
370		0.2	0.003	+0.002	0.001	10
380		0.2	0.000	+0.002	(-0.002)*	(-20)*

*Values Uncertain

TABLE VIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 15 PERCENT ETHYLENE GLYCOL–85 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/19/59	0.5	0.493	+0.117	0.376	3760
230		0.5	0.408	+0.026	0.382	3820
240		0.5	0.377	−0.003	0.380	3800
250		0.5	0.335	−0.001	0.336	3360
260		0.5	0.263	+0.003	0.260	2600
270		0.5	0.181	+0.003	0.178	1780
280		0.5	0.115	+0.003	0.112	1120
290		0.5	0.077	+0.002	0.075	750
300		0.5	0.062	+0.002	0.060	600
310		0.5	0.054	+0.002	0.052	520
320		0.5	0.053	+0.002	0.051	510
320	1/25/59	0.5	0.047	+0.001	0.046	460
330		0.5	0.046	+0.001	0.045	450
340		0.2	0.044	0.000	0.044	440
350		0.2	0.038	0.000	0.038	380
360		0.2	0.032	0.000	0.032	320
370		0.2	0.027	0.000	0.027	270
380		0.2	0.022	0.000	0.022	220
390		0.2	0.017	0.000	0.017	170
400		0.05	0.009	0.000	0.009	90

TABLE IX. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 35 PERCENT ETHYLENE GLYCOL-65 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/20/59	0.5	0.479	+0.112	0.367	3670
230		0.5	0.401	+0.019	0.382	3820
240		0.5	0.364	-0.008	0.372	3720
250		0.5	0.322	-0.006	0.328	3280
260		0.5	0.247	-0.002	0.249	2490
270		0.5	0.175	-0.001	0.176	1760
280		0.5	0.121	-0.001	0.122	1220
290		0.5	0.093	-0.001	0.094	940
300		0.5	0.078	-0.001	0.079	790
310		0.5	0.075	-0.001	0.076	760
320		0.5	0.076	-0.002	0.078	780
320	1/25/59	0.5	0.074	+0.001	0.073	730
330		0.5	0.078	+0.001	0.077	770
340		0.2	0.080	+0.001	0.079	790
350		0.2	0.077	+0.001	0.076	760
360		0.2	0.069	+0.001	0.068	680
370		0.2	0.062	+0.001	0.061	610
380		0.2	0.053	0.000	0.053	530
390		0.2	0.045	0.000	0.045	450
400		0.05	0.037	0.000	0.037	370

TABLE X. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 55 PERCENT ETHYLENE GLYCOL-45 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/20/59	0.5	0.459	+0.112	0.347	3470
230		0.5	0.380	+0.022	0.358	3580
240		0.5	0.344	-0.005	0.349	3490
250		0.5	0.300	-0.003	0.303	3030
260		0.5	0.237	+0.002	0.235	2350
270		0.5	0.172	+0.002	0.170	1700
280		0.5	0.126	+0.001	0.125	1250
290		0.5	0.099	+0.001	0.098	980
300		0.5	0.090	+0.001	0.089	890
310		0.5	0.098	+0.001	0.097	970
320		0.5	0.112	+0.001	0.111	1110
320	1/26/59	0.5	0.112	0.000	0.112	1120
330		0.5	0.126	0.000	0.126	1260
340		0.2	0.132	0.000	0.132	1320
350		0.2	0.134	0.000	0.134	1340
360		0.2	0.126	0.000	0.126	1260
370		0.2	0.114	0.000	0.114	1140
380		0.2	0.100	0.000	0.100	1000
390		0.2	0.085	0.000	0.085	850
400		0.05	0.066	0.000	0.066	660

TABLE XI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 75 PERCENT ETHYLENE GLYCOL-25 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/20/59	0.5	0.500	+0.114	0.386	3860
230		0.5	0.413	+0.022	0.391	3910
240		0.5	0.372	−0.005	0.377	3770
250		0.5	0.326	−0.003	0.329	3290
260		0.5	0.260	+0.001	0.259	2590
270		0.5	0.197	+0.002	0.195	1950
280		0.5	0.151	+0.001	0.150	1500
290		0.5	0.123	+0.001	0.122	1220
300		0.5	0.117	+0.001	0.116	1160
310		0.5	0.132	0.000	0.132	1320
320		0.5	0.154	0.000	0.154	1540
320	1/26/59	0.5	0.154	0.000	0.154	1540
330		0.5	0.178	0.000	0.178	1780
340		0.2	0.192	0.000	0.192	1920
350		0.2	0.194	0.000	0.194	1940
360		0.2	0.185	0.000	0.185	1850
370		0.2	0.169	0.000	0.169	1690
380		0.2	0.148	0.000	0.148	1480
390		0.2	0.127	0.000	0.127	1270
400		0.05	0.105	0.000	0.105	1050

TABLE XII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 90 PERCENT ETHYLENE GLYCOL-10 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/21/59	0.5	0.500	+0.118	0.382	3820
230		0.5	0.436	+0.024	0.412	4120
240		0.5	0.416	-0.005	0.421	4210
250		0.5	0.377	-0.002	0.379	3790
260		0.5	0.314	+0.001	0.313	3130
270		0.5	0.246	+0.001	0.245	2450
280		0.5	0.194	+0.001	0.193	1930
290		0.5	0.159	0.000	0.159	1590
300		0.5	0.152	0.000	0.152	1520
310		0.5	0.171	0.000	0.171	1710
320		0.5	0.197	0.000	0.197	1970
320	1/26/59	0.5	0.195	0.000	0.195	1950
330		0.5	0.227	0.000	0.227	2270
340		0.2	0.248	0.000	0.248	2480
350		0.2	0.254	0.000	0.254	2540
360		0.2	0.245	0.000	0.245	2450
370		0.2	0.224	0.000	0.224	2240
380		0.2	0.198	0.000	0.198	1980
390		0.2	0.168	0.000	0.168	1680
400		0.05	0.138	0.000	0.138	1380

TABLE XIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	ϵ_M
220	1/18/59	0.5	0.405	-0.016	0.421	4110
230		0.5	0.403	-0.017	0.420	4100
240		0.5	0.392	-0.026	0.418	4080
250		0.5	0.357	-0.018	0.375	3660
260		0.5	0.287	-0.008	0.295	2880
270		0.5	0.191	-0.003	0.194	1900
280		0.5	0.117	-0.002	0.119	1160
290		0.5	0.074	-0.002	0.076	740
300		0.5	0.051	-0.001	0.052	510
310		0.5	0.039	-0.001	0.040	390
320		0.5	0.030	-0.001	0.031	300
320	1/24/59	0.5	0.022	+0.001	0.021	210
330		0.5	0.014	0.000	0.014	140
340		0.2	0.007	0.000	0.007	70
350		0.2	0.006	0.000	0.006	60
360		0.2	0.001	0.000	0.001	10

TABLE XIV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 15 PERCENT ETHYLENE GLYCOL-85 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/21/59	0.5	0.367	-0.006	0.373	3640
230		0.5	0.352	-0.010	0.362	3540
240		0.5	0.320	-0.021	0.341	3330
250		0.5	0.276	-0.013	0.289	2820
260		0.5	0.215	-0.001	0.216	2110
270		0.5	0.147	+0.001	0.146	1430
280		0.5	0.102	+0.001	0.101	990
290		0.5	0.072	+0.001	0.071	690
300		0.5	0.058	+0.001	0.057	560
310		0.5	0.047	+0.001	0.046	450
320		0.5	0.045	+0.001	0.044	430
320	1/24/59	0.5	0.038	0.000	0.038	370
330		0.5	0.038	0.000	0.038	370
340		0.2	0.036	0.000	0.036	350
350		0.2	0.031	0.000	0.031	300
360		0.2	0.027	0.000	0.027	260
370		0.2	0.023	0.000	0.023	220
380		0.2	0.020	0.000	0.020	200
390		0.2	0.017	0.000	0.017	170
400		0.05	0.012	0.000	0.012	120

TABLE XV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 35 PERCENT ETHYLENE GLYCOL-65 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/21/59	0.5	0.277	-0.011	0.288	2820
230		0.5	0.277	-0.014	0.291	2840
240		0.5	0.277	-0.023	0.300	2930
250		0.5	0.244	-0.015	0.259	2530
260		0.5	0.185	-0.003	0.188	1840
270		0.5	0.124	-0.001	0.125	1220
280		0.5	0.090	0.000	0.090	880
290		0.5	0.074	-0.001	0.075	730
300		0.5	0.063	-0.001	0.064	630
310		0.5	0.067	0.000	0.067	650
320		0.5	0.067	0.000	0.067	650
320	1/24/59	0.5	0.067	0.000	0.067	650
330		0.5	0.073	0.000	0.073	710
340		0.2	0.074	0.000	0.074	720
350		0.2	0.072	0.000	0.072	700
360		0.2	0.066	0.000	0.066	650
370		0.2	0.058	0.000	0.058	570
380		0.2	0.051	0.000	0.051	510
390		0.2	0.043	0.000	0.043	420
400		0.05	0.036	0.000	0.036	350

TABLE XVI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 55 PERCENT ETHYLENE GLYCOL–45 PERCENT WATER. ($b = 0.998$ cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/22/59	0.7	0.322	−0.003	0.325	3170
230		0.5	0.320	−0.008	0.328	3200
240		0.5	0.295	−0.019	0.314	3070
250		0.5	0.248	−0.011	0.259	2530
260		0.5	0.184	0.000	0.184	1800
270		0.5	0.132	+0.003	0.129	1260
280		0.5	0.106	+0.002	0.104	1020
290		0.5	0.094	+0.002	0.092	900
300		0.5	0.092	+0.002	0.090	880
310		0.5	0.100	+0.002	0.098	960
320		0.5	0.107	+0.001	0.106	1040
320	1/25/59	0.5	0.101	+0.001	0.100	980
330		0.5	0.112	+0.001	0.111	1080
340		0.2	0.118	+0.001	0.117	1140
350		0.2	0.119	+0.001	0.118	1150
360		0.2	0.112	+0.001	0.111	1080
370		0.2	0.102	0.000	0.102	1000
380		0.2	0.090	0.000	0.090	880
390		0.2	0.077	0.000	0.077	750
400		0.05	0.063	0.000	0.063	620

TABLE XVII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 75 PERCENT ETHYLENE GLYCOL-25 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/22/59	0.7	0.453	-0.018	0.471	4600
230		0.5	0.436	-0.018	0.454	4440
240		0.5	0.370	-0.026	0.396	3870
250		0.5	0.311	-0.018	0.329	3210
260		0.5	0.249	-0.006	0.255	2490
270		0.5	0.193	-0.003	0.196	1910
280		0.5	0.144	+0.002	0.146	1430
290		0.5	0.118	-0.002	0.120	1170
300		0.5	0.117	-0.002	0.119	1160
310		0.5	0.131	-0.001	0.132	1290
320		0.5	0.149	-0.001	0.150	1470
320	1/25/59	0.5	0.147	0.000	0.147	1440
330		0.5	0.168	0.000	0.168	1640
340		0.2	0.181	0.000	0.181	1770
350		0.2	0.184	0.000	0.184	1800
360		0.2	0.176	0.000	0.176	1720
370		0.2	0.161	0.000	0.161	1570
380		0.2	0.141	0.000	0.141	1380
390		0.2	0.122	0.000	0.122	1190
400		0.05	0.100	0.000	0.100	980

TABLE XVIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 90 PERCENT ETHYLENE GLYCOL-10 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	1/22/59	0.7	0.384	-0.013	0.397	3880
230		0.7	0.385	-0.024	0.409	4000
240		0.5	0.338	-0.017	0.355	3470
250		0.5	0.277	-0.005	0.282	2760
260		0.5	0.224	-0.002	0.226	2210
270		0.5	0.191	-0.002	0.193	1890
280		0.5	0.176	-0.002	0.178	1740
290		0.5	0.155	-0.002	0.157	1530
300		0.5	0.142	-0.002	0.146	1430
310		0.5	0.154	-0.002	0.156	1520
320		0.5	0.181	-0.002	0.183	1790
320	1/25/59	0.5	0.179	0.000	0.179	1750
330		0.5	0.207	0.000	0.207	2020
340		0.2	0.226	0.000	0.226	2210
350		0.2	0.233	0.000	0.233	2280
360		0.2	0.225	0.000	0.225	2220
370		0.2	0.211	0.000	0.211	2060
380		0.2	0.183	0.000	0.183	1790
390		0.2	0.156	0.000	0.156	1520
400		0.2	0.128	0.000	0.128	1250

TABLE XIX. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
240	2/11/59	0.5	2.65	-0.005	2.66	2650
250		0.5	2.80	-0.003	2.80	2790
260		0.5	2.80	+0.001	2.80	2790
270		0.5	1.915	+0.002	1.913	1910
280		0.5	1.197	+0.001	1.196	1190
290		0.5	0.748	+0.001	0.747	750
300		0.5	0.537	0.000	0.537	540
310		0.5	0.465	+0.001	0.464	460
320		0.5	0.511	+0.001	0.510	510
320		0.5	0.509	0.000	0.509	510
330		0.5	0.542	0.000	0.542	540
340		0.2	0.500	0.000	0.500	500
350		0.2	0.386	-0.001	0.387	390
360		0.2	0.246	-0.001	0.247	250
370		0.2	0.136	-0.001	0.137	140
380		0.2	0.070	-0.001	0.071	70

TABLE XX. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 15 PERCENT ETHYLENE GLYCOL–85 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
230	2/8/59	0.5	2.90	+0.025	2.93	2920
240		0.5	2.61	-0.003	2.61	2600
250		0.5	2.61	-0.001	2.61	2600
260		0.5	2.45	+0.003	2.45	2440
270		0.5	1.668	+0.003	1.665	1660
280		0.5	1.037	+0.003	1.034	1030
290		0.5	0.651	+0.002	0.649	650
300		0.5	0.479	+0.002	0.477	480
310		0.5	0.438	+0.002	0.436	430
320		0.5	0.456	+0.001	0.455	450
320		0.5	0.454	0.000	0.454	450
330		0.5	0.494	0.000	0.494	490
340		0.2	0.459	0.000	0.459	460
350		0.2	0.394	0.000	0.394	390
360		0.2	0.299	0.000	0.299	300
370		0.2	0.216	0.000	0.216	220
380		0.2	0.159	0.000	0.159	160
390		0.2	0.121	0.000	0.121	120
400		0.05	0.091	0.000	0.091	90

TABLE XXI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 35 PERCENT ETHYLENE GLYCOL-65 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
260	2/8/59	0.5	2.59	-0.004	2.59	2580
270		0.5	1.750	-0.002	1.752	1750
280		0.5	1.161	-0.002	1.163	1160
290		0.5	0.778	-0.002	0.780	780
300		0.5	0.617	-0.002	0.619	620
310		0.5	0.606	-0.002	0.608	610
320		0.5	0.672	-0.002	0.674	670
320		0.5	0.673	+0.002	0.671	670
330		0.5	0.742	+0.002	0.740	740
340		0.2	0.749	+0.002	0.747	750
350		0.2	0.682	+0.001	0.681	680
360		0.2	0.575	+0.001	0.574	570
370		0.2	0.462	+0.001	0.461	460
380		0.2	0.385	+0.001	0.384	380
400		0.05	0.251	+0.001	0.250	250

TABLE XXII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 55 PERCENT ETHYLENE GLYCOL–45 PERCENT WATER. ($b = 0.097$ cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
260	2/8/59	0.5	2.62	0.000	2.62	2610
270		0.5	1.94	+0.001	1.94	1930
280		0.5	1.372	0.000	1.372	1370
290		0.5	1.005	0.000	1.005	1000
300		0.5	0.860	0.000	0.860	860
310		0.5	0.900	0.000	0.900	900
320		0.5	1.042	0.000	1.042	1040
320		0.5	1.038	+0.002	1.036	1030
330		0.5	1.188	+0.002	1.186	1180
340		0.2	1.249	+0.002	1.247	1240
350		0.2	1.194	+0.002	1.192	1190
360		0.2	1.071	+0.002	1.069	1070
370		0.2	0.920	+0.002	0.918	920
380		0.2	0.783	+0.002	0.781	780
390		0.2	0.660	+0.002	0.658	660
400		0.05	0.537	+0.001	0.536	530

TABLE XXIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 75 PERCENT ETHYLENE GLYCOL-25 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
260	2/9/59	0.5	3.0	+0.001	3.0	2990
270		0.5	2.14	+0.001	2.14	2140
280		0.5	1.585	+0.001	1.584	1580
290		0.5	1.229	0.000	1.229	1220
300		0.5	1.116	+0.001	1.115	1110
310		0.5	1.204	+0.001	1.203	1200
320		0.5	1.390	0.000	1.390	1390
320		0.5	1.390	0.000	1.390	1390
330		0.5	1.578	0.000	1.578	1570
340		0.2	1.688	0.000	1.688	1680
350		0.2	1.678	0.000	1.678	1670
360		0.2	1.552	0.000	1.552	1550
370		0.2	1.386	0.000	1.386	1380
380		0.2	1.202	0.000	1.202	1200
390		0.2	1.018	0.000	1.018	1010
400		0.05	0.825	0.000	0.825	820

TABLE XXIV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 90 PERCENT ETHYLENE GLYCOL-10 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
260	2/9/59	0.5	2.95	+0.002	2.95	2940
270		0.5	2.42	+0.002	2.42	2410
280		0.5	1.845	+0.002	1.843	1840
290		0.5	1.515	+0.003	1.512	1510
300		0.5	1.406	+0.003	1.403	1400
310		0.5	1.542	+0.003	1.539	1530
320		0.5	1.798	+0.003	1.795	1790
320		0.5	1.795	0.000	1.795	1790
330		0.5	2.08	0.000	2.08	2070
340		0.2	2.33	0.000	2.33	2320
350		0.2	2.37	0.000	2.37	2360
360		0.2	2.16	0.000	2.16	2150
370		0.2	1.96	0.000	1.96	1950
380		0.2	1.720	0.000	1.720	1710
390		0.2	1.451	0.000	1.451	1450
400		0.05	1.190	0.000	1.190	1190

TABLE XXV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
260	2/8/59	0.5	2.73	-0.008	2.74	2670
270		0.5	1.785	-0.003	1.788	1740
280		0.5	1.087	-0.002	1.089	1060
290		0.5	0.678	-0.002	0.680	660
300		0.5	0.480	-0.001	0.481	470
310		0.5	0.385	-0.001	0.386	380
320		0.5	0.324	-0.001	0.325	320
320		0.8	0.323	+0.001	0.322	310
330		0.5	0.268	0.000	0.268	260
340		0.2	0.206	0.000	0.206	200
350		0.2	0.145	0.000	0.145	140
360		0.2	0.092	0.000	0.092	90
370		0.2	0.051	0.000	0.051	50
380		0.2	0.027	0.000	0.027	26
390		0.2	0.014	0.000	0.014	10
400		0.05	0.007	0.000	0.007	10

TABLE XXVI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 15 PERCENT ETHYLENE GLYCOL–85 PERCENT WATER. ($b = 0.097$ cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/8/59	0.5	0.481	+0.117	0.364	3640
230		0.5	0.399	+0.026	0.373	3730
240		0.5	0.368	−0.003	0.371	3710
250		0.5	0.329	−0.001	0.330	3300
260		0.5	0.256	+0.003	0.253	2530
270		0.5	0.174	+0.003	0.171	1710
280		0.5	0.111	+0.003	0.108	1080
290		0.5	0.074	+0.002	0.072	720
300		0.5	0.057	+0.002	0.055	550
310		0.5	0.050	+0.002	0.048	480
320		0.5	0.049	+0.002	0.047	470
320		0.5	0.047	+0.001	0.046	460
330		0.5	0.045	+0.001	0.044	440
340		0.2	0.042	0.000	0.042	420
350		0.2	0.037	0.000	0.037	370
360		0.2	0.032	0.000	0.032	320
370		0.2	0.026	0.000	0.026	260
380		0.2	0.022	0.000	0.022	220
390		0.2	0.017	0.000	0.017	170
400		0.05	0.013	0.000	0.013	130

TABLE XXVII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030 x 10^{-3} MOLAR IRON (III) PERCHLORATE IN 35 PERCENT ETHYLENE GLYCOL-65 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/8/59	0.5	0.465	+0.112	0.353	3530
230		0.5	0.383	+0.019	0.364	3640
240		0.5	0.348	-0.008	0.356	3560
250		0.5	0.303	-0.006	0.309	3090
260		0.5	0.237	-0.002	0.239	2390
270		0.5	0.166	-0.001	0.167	1670
280		0.5	0.112	-0.001	0.113	1130
290		0.5	0.082	-0.001	0.083	830
300		0.5	0.069	-0.001	0.070	700
310		0.5	0.068	-0.001	0.070	700
320		0.5	0.074	-0.002	0.076	760
320		0.5	0.073	+0.001	0.072	720
330		0.5	0.078	+0.001	0.077	770
340		0.2	0.079	+0.001	0.078	780
350		0.2	0.076	+0.001	0.075	750
360		0.2	0.069	+0.001	0.068	680
370		0.2	0.061	+0.001	0.060	600
380		0.2	0.052	0.000	0.052	520
390		0.2	0.043	0.000	0.043	430
400		0.05	0.034	0.000	0.034	340

TABLE XXVIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 55 PERCENT ETHYLENE GLYCOL-45 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/9/59	0.5	0.459	+0.112	0.347	3470
230		0.5	0.375	+0.022	0.353	3530
240		0.5	0.334	-0.005	0.339	3390
250		0.5	0.290	-0.003	0.293	2930
260		0.5	0.229	+0.002	0.227	2270
270		0.5	0.167	+0.002	0.165	1650
280		0.5	0.121	+0.001	0.120	1200
290		0.5	0.095	+0.001	0.094	940
300		0.5	0.086	+0.001	0.085	850
310		0.5	0.092	+0.001	0.091	910
320		0.5	0.104	+0.001	0.103	1030
320		0.5	0.102	0.000	0.102	1020
330		0.5	0.114	0.000	0.114	1140
340		0.2	0.120	0.000	0.120	1200
350		0.2	0.120	0.000	0.120	1200
360		0.2	0.112	0.000	0.112	1120
370		0.2	0.101	0.000	0.101	1010
380		0.2	0.088	0.000	0.088	880
390		0.2	0.074	0.000	0.074	740
400		0.05	0.062	0.000	0.062	620

TABLE XXIX. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 75 PERCENT ETHYLENE GLYCOL-25 PERCENT WATER. ($b = 0.097$ cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/8/59	0.5	0.462	+0.114	0.348	3480
230		0.5	0.394	+0.022	0.372	3720
240		0.5	0.358	-0.005	0.363	3630
250		0.5	0.315	-0.003	0.318	3180
260		0.5	0.251	+0.001	0.250	2500
270		0.5	0.192	+0.002	0.190	1900
280		0.5	0.144	+0.001	0.143	1430
290		0.5	0.118	+0.001	0.117	1170
300		0.5	0.113	+0.001	0.112	1120
310		0.5	0.126	0.000	0.126	1260
320		0.5	0.146	0.000	0.146	1460
320		0.5	0.146	0.000	0.146	1460
330		0.5	0.165	0.000	0.165	1650
340		0.2	0.178	0.000	0.178	1780
350		0.2	0.181	0.000	0.181	1810
360		0.2	0.172	0.000	0.172	1720
370		0.2	0.156	0.000	0.156	1560
380		0.2	0.136	0.000	0.136	1360
390		0.2	0.118	0.000	0.118	1180
400		0.05	0.098	0.000	0.098	980

TABLE XXX. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 90 PERCENT ETHYLENE GLYCOL-10 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/9/59	0.5	0.501	+0.118	0.383	3830
230		0.5	0.437	+0.024	0.413	4130
240		0.5	0.411	-0.005	0.416	4160
250		0.5	0.376	-0.002	0.378	3780
260		0.5	0.316	+0.001	0.315	3150
270		0.5	0.247	+0.001	0.248	2480
280		0.5	0.192	+0.001	0.193	1930
290		0.5	0.158	0.000	0.158	1580
300		0.5	0.150	0.000	0.150	1500
310		0.5	0.167	0.000	0.167	1670
320		0.5	0.197	0.000	0.197	1970
320		0.5	0.197	0.000	0.197	1970
330		0.5	0.227	0.000	0.227	2270
340		0.2	0.247	0.000	0.247	2470
350		0.2	0.252	0.000	0.252	2520
360		0.2	0.242	0.000	0.242	2420
370		0.2	0.222	0.000	0.222	2220
380		0.2	0.195	0.000	0.195	1950
390		0.2	0.166	0.000	0.166	1660
400		0.05	0.138	0.000	0.138	1380

TABLE XXXI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/8/59	0.5	0.331	-0.016	0.347	3390
230		0.5	0.342	-0.017	0.359	3510
240		0.5	0.336	-0.026	0.362	3540
250		0.5	0.305	-0.018	0.323	3160
260		0.5	0.238	-0.008	0.246	2400
270		0.5	0.156	-0.003	0.159	1550
280		0.5	0.094	-0.002	0.096	940
290		0.5	0.058	-0.002	0.060	590
300		0.5	0.040	-0.001	0.041	400
310		0.5	0.031	-0.001	0.032	310
320		0.5	0.024	-0.001	0.025	240
320		0.5	0.022	+0.001	0.021	210
330		0.5	0.015	0.000	0.015	150
340		0.2	0.009	0.000	0.009	90
350		0.2	0.005	0.000	0.005	50
360		0.2	0.001	0.000	0.001	10

TABLE XXXII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 15 PERCENT ETHYLENE GLYCOL-85 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/8/59	0.5	0.301	-0.006	0.307	3000
230		0.5	0.306	-0.010	0.316	3090
240		0.5	0.291	-0.021	0.312	3050
250		0.5	0.254	-0.013	0.267	2610
260		0.5	0.192	-0.001	0.193	1890
270		0.5	0.133	+0.001	0.132	1290
280		0.5	0.089	+0.001	0.088	860
290		0.5	0.060	+0.001	0.059	580
300		0.5	0.047	+0.001	0.046	450
310		0.5	0.041	+0.001	0.040	390
320		0.5	0.039	+0.001	0.038	370
320		0.5	0.038	0.000	0.038	370
330		0.5	0.036	0.000	0.036	350
340		0.2	0.033	0.000	0.033	320
350		0.2	0.030	0.000	0.030	290
360		0.2	0.026	0.000	0.026	250
370		0.2	0.023	0.000	0.023	220
380		0.2	0.018	0.000	0.018	180
390		0.2	0.014	0.000	0.014	140
400		0.05	0.012	0.000	0.012	120

TABLE XXXIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 35 PERCENT ETHYLENE GLYCOL-65 PERCENT WATER. (b = 0.988 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/8/59	0.6	0.281	-0.011	0.292	2860
230		0.5	0.280	-0.014	0.294	2880
240		0.5	0.274	-0.023	0.297	2900
250		0.5	0.232	-0.015	0.247	2420
260		0.5	0.168	-0.003	0.171	1670
270		0.5	0.113	-0.001	0.114	1110
280		0.5	0.083	0.000	0.083	810
290		0.5	0.064	-0.001	0.065	640
300		0.5	0.058	-0.001	0.059	580
310		0.5	0.060	0.000	0.060	590
320		0.5	0.065	0.000	0.065	640
320		0.5	0.064	0.000	0.064	630
330		0.5	0.068	0.000	0.068	660
340		0.2	0.069	0.000	0.069	670
350		0.2	0.068	0.000	0.068	660
360		0.2	0.063	0.000	0.063	620
370		0.2	0.057	0.000	0.057	560
380		0.2	0.048	0.000	0.048	470
390		0.2	0.040	0.000	0.040	390
400		0.05	0.034	0.000	0.034	330

TABLE XXXIV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 55 PERCENT ETHYLENE GLYCOL-45 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/8/59	0.5	0.325	-0.003	0.328	3210
230		0.5	0.301	-0.008	0.309	3020
240		0.5	0.272	-0.019	0.291	2840
250		0.5	0.209	-0.011	0.220	2150
260		0.5	0.138	0.000	0.138	1350
270		0.5	0.096	+0.003	0.093	910
280		0.5	0.084	+0.002	0.082	800
290		0.5	0.077	+0.002	0.075	730
300		0.5	0.075	+0.002	0.073	710
310		0.5	0.083	+0.002	0.081	790
320		0.5	0.095	+0.001	0.094	920
320		0.5	0.097	+0.001	0.096	940
330		0.5	0.108	+0.001	0.107	1050
340		0.2	0.116	+0.001	0.115	1120
350		0.2	0.116	+0.001	0.115	1120
360		0.2	0.109	+0.001	0.108	1060
370		0.2	0.099	0.000	0.099	970
380		0.2	0.087	0.000	0.087	850
390		0.2	0.073	0.000	0.073	710
400		0.05	0.059	0.000	0.059	580

TABLE XXXV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 75 PERCENT ETHYLENE GLYCOL-25 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/9/59	0.8	0.351	-0.018	0.369	3610
230		0.5	0.342	-0.018	0.360	3520
240		0.5	0.310	-0.026	0.336	3280
250		0.5	0.265	-0.018	0.283	2760
260		0.5	0.210	-0.006	0.216	2110
270		0.5	0.156	-0.003	0.159	1550
280		0.5	0.123	-0.002	0.125	1220
290		0.5	0.105	-0.002	0.107	1050
300		0.5	0.104	-0.002	0.106	1040
310		0.5	0.121	-0.001	0.122	1190
320		0.5	0.143	-0.001	0.144	1410
320		0.5	0.142	0.000	0.142	1390
330		0.5	0.163	0.000	0.163	1590
340		0.2	0.177	0.000	0.177	1730
350		0.2	0.179	0.000	0.179	1750
360		0.2	0.171	0.000	0.171	1670
370		0.2	0.157	0.000	0.157	1530
380		0.2	0.138	0.000	0.138	1350
390		0.2	0.118	0.000	0.118	1150
400		0.05	0.097	0.000	0.097	950

TABLE XXXVI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 90 PERCENT ETHYLENE GLYCOL-10 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/9/59	0.8	0.241	-0.013	0.254	2530
230		0.5	0.281	-0.024	0.305	2980
240		0.5	0.284	-0.017	0.301	2950
250		0.5	0.260	-0.005	0.265	2590
260		0.5	0.218	-0.002	0.220	2150
270		0.5	0.176	-0.002	0.178	1740
280		0.5	0.150	-0.002	0.152	1470
290		0.5	0.132	-0.002	0.134	1310
300		0.5	0.126	-0.002	0.128	1250
310		0.5	0.142	-0.002	0.144	1410
320		0.5	0.171	-0.002	0.173	1690
320		0.5	0.166	0.000	0.166	1620
330		0.5	0.194	0.000	0.194	1890
340		0.2	0.213	0.000	0.213	2080
350		0.2	0.218	0.000	0.218	2130
360		0.2	0.210	0.000	0.210	2050
370		0.2	0.193	0.000	0.193	1880
380		0.2	0.170	0.000	0.170	1660
390		0.2	0.144	0.000	0.144	1410
400		0.05	0.118	0.000	0.118	1150

TABLE XXXVII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
240	2/21/59	0.5	2.60	-0.005	2.61	2600
250		0.5	2.65	-0.003	2.65	2640
260		0.5	2.65	+0.001	2.65	2640
270		0.5	1.940	+0.002	1.938	1930
280		0.5	1.198	+0.001	1.197	1190
290		0.5	0.742	+0.001	0.741	740
300		0.5	0.532	0.000	0.532	530
310		0.5	0.472	+0.001	0.471	470
320		0.5	0.509	+0.001	0.508	510
320		0.5	0.509	0.000	0.509	510
330		0.5	0.541	0.000	0.541	540
340		0.2	0.504	0.000	0.504	500
350		0.2	0.387	0.000	0.387	390
360		0.2	0.243	-0.001	0.244	240
370		0.2	0.136	-0.001	0.137	140
380		0.2	0.070	-0.001	0.071	70
390		0.2	0.037	-0.001	0.038	40
400		0.05	0.018	-0.001	0.019	20

TABLE XXXVIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 15 PERCENT ETHYLENE GLYCOL–85 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
240	2/23/59	0.5	2.84	-0.003	2.84	2830
250		0.5	2.84	-0.001	2.84	2830
260		0.5	2.14	+0.003	2.14	2140
270		0.5	1.483	+0.003	1.480	1480
280		0.5	0.915	+0.003	0.912	910
290		0.5	0.580	+0.002	0.578	580
300		0.5	0.423	+0.002	0.421	420
310		0.5	0.377	+0.002	0.375	370
320		0.5	0.388	+0.001	0.387	390
320		0.5	0.385	0.000	0.385	380
330		0.5	0.403	0.000	0.403	400
340		0.2	0.390	0.000	0.390	390
350		0.2	0.326	0.000	0.326	330
360		0.2	0.250	0.000	0.250	250
370		0.2	0.184	0.000	0.184	180
380		0.2	0.137	0.000	0.137	140
390		0.2	0.105	0.000	0.105	110
400		0.05	0.080	0.000	0.080	80

TABLE XXXIX. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 35 PERCENT ETHYLENE GLYCOL-65 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
260	2/23/59	0.5	2.12	-0.004	2.12	2110
270		0.5	1.501	-0.002	1.503	1500
280		0.5	0.975	-0.002	0.977	970
290		0.5	0.651	-0.002	0.653	650
300		0.5	0.505	-0.002	0.507	510
310		0.5	0.498	-0.002	0.500	500
320		0.5	0.542	-0.002	0.544	540
320		0.5	0.541	+0.002	0.539	540
330		0.5	0.592	+0.002	0.590	590
340		0.2	0.599	+0.002	0.597	600
350		0.2	0.550	+0.001	0.549	550
360		0.2	0.469	+0.001	0.468	470
370		0.2	0.385	+0.001	0.384	380
380		0.2	0.316	+0.001	0.315	310
390		0.2	0.259	+0.001	0.258	260
400		0.05	0.207	+0.001	0.206	210

TABLE XL. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 55 PERCENT ETHYLENE GLYCOL-45 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
250	2/21/59	0.5	2.82	-0.003	2.82	2810
260		0.5	2.35	0.000	2.35	2340
270		0.5	1.757	+0.001	1.756	1750
280		0.5	1.248	0.000	1.248	1240
290		0.5	0.900	0.000	0.900	900
300		0.5	0.782	0.000	0.782	780
310		0.5	0.810	0.000	0.810	810
320		0.5	0.930	0.000	0.930	930
320		0.5	0.925	+0.002	0.923	920
330		0.5	1.053	+0.002	1.051	1050
340		0.2	1.108	+0.002	1.106	1100
350		0.2	1.057	+0.002	1.055	1050
360		0.2	0.950	+0.002	0.948	950
370		0.2	0.830	+0.002	0.828	830
380		0.2	0.711	+0.002	0.709	710
390		0.2	0.599	+0.002	0.597	600
400		0.05	0.494	+0.001	0.493	490

TABLE XLI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 75 PERCENT ETHYLENE GLYCOL-25 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
260	2/23/59	0.5	2.48	+0.001	2.48	2400
270		0.5	1.940	+0.001	1.939	1930
280		0.5	1.444	+0.001	1.443	1440
290		0.5	1.124	0.000	1.124	1120
300		0.5	1.021	+0.001	1.020	1020
310		0.5	1.094	+0.001	1.093	1090
320		0.5	1.269	0.000	1.269	1270
320		0.5	1.269	0.000	1.269	1270
330		0.5	1.452	0.000	1.452	1450
340		0.2	1.550	0.000	1.550	1550
350		0.2	1.530	0.000	1.530	1530
360		0.2	1.423	0.000	1.423	1420
370		0.2	1.270	0.000	1.270	1270
380		0.2	1.102	0.000	1.102	1100
390		0.2	0.925	0.000	0.925	920
400		0.05	0.762	0.000	0.762	760

TABLE XLII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.034×10^{-2} MOLAR IRON (III) PERCHLORATE IN 90 PERCENT ETHYLENE GLYCOL-10 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
260	2/21/59	0.5	2.73	+0.002	2.73	2720
270		0.5	2.26	+0.002	2.26	2260
280		0.5	1.742	+0.002	1.740	1740
290		0.5	1.409	+0.003	1.406	1400
300		0.5	1.312	+0.003	1.309	1300
310		0.5	1.428	+0.003	1.425	1420
320		0.5	1.673	+0.003	1.670	1670
320		0.5	1.670	0.000	1.670	1670
330		0.5	1.935	0.000	1.935	1930
340		0.2	2.08	0.000	2.08	2080
350		0.2	2.13	0.000	2.13	2130
360		0.2	2.00	0.000	2.00	2000
370		0.2	1.815	0.000	1.815	1810
380		0.2	1.588	0.000	1.588	1580
390		0.2	1.349	0.000	1.349	1350
400		0.05	1.114	0.000	1.114	1110

TABLE XLIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
260	2/21/59	0.5	2.60	-0.008	2.61	2540
270		0.5	1.790	-0.003	1.793	1750
280		0.5	1.088	-0.002	1.090	1060
290		0.5	0.678	-0.002	0.680	660
300		0.5	0.479	-0.001	0.480	470
310		0.5	0.382	-0.001	0.383	370
320		0.5	0.323	-0.001	0.324	320
320		0.5	0.329	+0.001	0.328	320
330		0.5	0.272	0.000	0.272	270
340		0.2	0.211	0.000	0.211	210
350		0.2	0.148	0.000	0.148	140
360		0.2	0.091	0.000	0.091	90
370		0.2	0.049	0.000	0.049	50
380		0.2	0.026	0.000	0.026	30
390		0.2	0.013	0.000	0.013	10
400		0.05	0.007	0.000	0.007	10

TABLE XLIV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 15 PERCENT ETHYLENE GLYCOL–85 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/23/59	0.5	0.491	+0.117	0.374	3740
230		0.5	0.401	+0.026	0.375	3750
240		0.5	0.369	-0.003	0.372	3720
250		0.5	0.329	-0.001	0.330	3300
260		0.5	0.257	+0.003	0.254	2540
270		0.5	0.176	+0.003	0.173	1730
280		0.5	0.113	+0.003	0.110	1100
290		0.5	0.076	+0.002	0.074	740
300		0.5	0.059	+0.002	0.057	570
310		0.5	0.051	+0.002	0.049	490
320		0.5	0.050	+0.002	0.048	480
320		0.5	0.050	+0.001	0.049	490
330		0.5	0.047	+0.001	0.046	460
340		0.2	0.044	0.000	0.044	440
350		0.2	0.038	0.000	0.038	380
360		0.2	0.032	0.000	0.032	320
370		0.2	0.026	0.000	0.026	260
380		0.2	0.022	0.000	0.022	220
390		0.2	0.018	0.000	0.018	180
400		0.05	0.015	0.000	0.015	150

TABLE XLV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 35 PERCENT ETHYLENE GLYCOL-65 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/26/59	0.5	0.472	+0.112	0.360	3600
230		0.5	0.381	+0.019	0.362	3620
240		0.5	0.340	-0.008	0.348	3480
250		0.5	0.297	-0.006	0.303	3030
260		0.5	0.234	-0.002	0.236	2360
270		0.5	0.164	-0.001	0.165	1650
280		0.5	0.112	-0.001	0.113	1130
290		0.5	0.082	-0.001	0.083	830
300		0.5	0.069	-0.001	0.070	700
310		0.5	0.069	-0.001	0.070	700
320		0.5	0.074	-0.002	0.076	760
320		0.5	0.073	+0.001	0.072	720
330		0.5	0.076	+0.001	0.075	750
340		0.2	0.079	+0.001	0.078	780
350		0.2	0.075	+0.001	0.074	740
360		0.2	0.068	+0.001	0.067	670
370		0.2	0.061	+0.001	0.060	600
380		0.2	0.051	0.000	0.051	510
390		0.2	0.043	0.000	0.043	430
400		0.05	0.036	0.000	0.036	360

TABLE XLVI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 55 PERCENT ETHYLENE GLYCOL-45 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/21/59	0.5	0.445	+0.112	0.333	3330
230		0.5	0.357	+0.022	0.335	3350
240		0.5	0.316	-0.005	0.321	3210
250		0.5	0.271	-0.003	0.274	2740
260		0.5	0.210	+0.002	0.208	2080
270		0.5	0.154	+0.002	0.152	1520
280		0.5	0.111	+0.001	0.110	1100
290		0.5	0.086	+0.001	0.085	850
300		0.5	0.080	+0.001	0.079	790
310		0.5	0.087	+0.001	0.086	860
320		0.5	0.098	+0.001	0.097	970
320		0.5	0.098	0.000	0.098	980
330		0.5	0.109	0.000	0.109	1090
340		0.2	0.115	0.000	0.115	1150
350		0.2	0.114	0.000	0.114	1140
360		0.2	0.107	0.000	0.107	1070
370		0.2	0.096	0.000	0.096	960
380		0.2	0.084	0.000	0.084	840
390		0.2	0.072	0.000	0.072	720
400		0.05	0.062	0.000	0.062	620

TABLE XLVII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 75 PERCENT ETHYLENE GLYCOL-25 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/26/59	0.5	0.429	+0.114	0.315	3150
230		0.5	0.370	+0.022	0.348	3480
240		0.5	0.336	-0.005	0.341	3410
250		0.5	0.296	-0.003	0.299	2990
260		0.5	0.238	+0.001	0.237	2370
270		0.5	0.179	+0.002	0.177	1770
280		0.5	0.135	+0.001	0.134	1340
290		0.5	0.110	+0.001	0.109	1090
300		0.5	0.106	+0.001	0.105	1050
310		0.5	0.119	0.000	0.119	1190
320		0.5	0.139	0.000	0.139	1390
320		0.5	0.137	0.000	0.137	1370
330		0.5	0.158	0.000	0.158	1580
340		0.2	0.171	0.000	0.171	1710
350		0.2	0.172	0.000	0.172	1720
360		0.2	0.164	0.000	0.164	1640
370		0.2	0.149	0.000	0.149	1490
380		0.2	0.131	0.000	0.131	1310
390		0.2	0.111	0.000	0.111	1110
400		0.05	0.093	0.000	0.093	930

TABLE XLVIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.030×10^{-3} MOLAR IRON (III) PERCHLORATE IN 90 PERCENT ETHYLENE GLYCOL-10 PERCENT WATER. (b = 0.097 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/21/59	0.5	0.472	+0.118	0.354	3540
230		0.5	0.407	+0.024	0.383	3830
240		0.5	0.389	-0.005	0.394	3940
250		0.5	0.361	-0.002	0.363	3630
260		0.5	0.304	+0.001	0.303	3030
270		0.5	0.237	+0.001	0.236	2360
280		0.5	0.183	+0.001	0.182	1820
290		0.5	0.150	0.000	0.150	1500
300		0.5	0.145	0.000	0.145	1450
310		0.5	0.162	0.000	0.162	1620
320		0.5	0.193	0.000	0.193	1930
320		0.5	0.192	0.000	0.192	1920
330		0.5	0.222	0.000	0.222	2220
340		0.2	0.241	0.000	0.241	2410
350		0.2	0.247	0.000	0.247	2470
360		0.2	0.283	0.000	0.283	2830
370		0.2	0.216	0.000	0.216	2160
380		0.2	0.189	0.000	0.189	1890
390		0.2	0.163	0.000	0.163	1630
400		0.05	0.136	0.000	0.136	1360

TABLE XLIX. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/21/59	0.5	0.333	-0.016	0.349	3410
230		0.5	0.343	-0.017	0.360	3520
240		0.5	0.352	-0.026	0.378	3690
250		0.5	0.305	-0.018	0.323	3150
260		0.5	0.220	-0.008	0.228	2210
270		0.5	0.137	-0.003	0.140	1370
280		0.5	0.082	-0.002	0.084	820
290		0.5	0.050	-0.002	0.052	510
300		0.5	0.034	-0.001	0.035	340
310		0.5	0.027	-0.001	0.028	270
320		0.5	0.019	-0.001	0.020	200
320		0.5	0.018	+0.001	0.017	170
330		0.5	0.012	0.000	0.012	120
340		0.2	0.006	0.000	0.006	60
350		0.2	0.001	0.000	0.001	10

TABLE L. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 15 PERCENT ETHYLENE GLYCOL-85 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/23/59	0.5	0.311	-0.006	0.317	3100
230		0.5	0.312	-0.010	0.322	3140
240		0.5	0.292	-0.021	0.313	3060
250		0.5	0.256	-0.013	0.269	2620
260		0.5	0.198	-0.001	0.199	1940
270		0.5	0.134	+0.001	0.133	1330
280		0.5	0.088	+0.001	0.087	850
290		0.5	0.065	+0.001	0.064	620
300		0.5	0.047	+0.001	0.046	450
310		0.5	0.042	+0.001	0.041	400
320		0.5	0.039	+0.001	0.038	370
320		0.5	0.038	0.000	0.038	370
330		0.5	0.036	0.000	0.036	350
340		0.2	0.034	0.000	0.034	330
350		0.2	0.030	0.000	0.030	290
360		0.2	0.027	0.000	0.027	260
370		0.2	0.023	0.000	0.023	220
380		0.2	0.021	0.000	0.021	210
390		0.2	0.015	0.000	0.015	150
400		0.05	0.012	0.000	0.012	120

TABLE LI. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 35 PERCENT ETHYLENE GLYCOL–65 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/26/59	0.6	0.306	-0.011	0.317	3100
230		0.5	0.295	-0.014	0.309	3020
240		0.5	0.273	-0.023	0.296	2890
250		0.5	0.223	-0.015	0.238	2320
260		0.5	0.156	-0.003	0.159	1550
270		0.5	0.103	-0.001	0.104	1020
280		0.5	0.076	0.000	0.076	740
290		0.5	0.060	-0.001	0.061	600
300		0.5	0.055	-0.001	0.056	550
310		0.5	0.058	0.000	0.058	570
320		0.5	0.064	0.000	0.064	620
320		0.5	0.064	0.000	0.064	620
330		0.5	0.069	0.000	0.069	670
340		0.2	0.071	0.000	0.071	690
350		0.2	0.069	0.000	0.069	670
360		0.2	0.064	0.000	0.064	620
370		0.2	0.057	0.000	0.057	560
380		0.2	0.049	0.000	0.049	480
390		0.2	0.042	0.000	0.042	410
400		0.05	0.034	0.000	0.034	330

TABLE LII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 55 PERCENT ETHYLENE GLYCOL-45 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/21/59	0.6	0.381	-0.003	0.384	3750
230		0.5	0.337	-0.008	0.345	3370
240		0.5	0.282	-0.019	0.301	2940
250		0.5	0.212	-0.011	0.223	2180
260		0.5	0.138	0.000	0.138	1350
270		0.5	0.098	+0.003	0.095	930
280		0.5	0.089	+0.002	0.087	850
290		0.5	0.080	+0.002	0.078	760
300		0.5	0.078	+0.002	0.076	740
310		0.5	0.088	+0.002	0.086	840
320		0.5	0.100	+0.001	0.099	970
320		0.5	0.100	+0.001	0.099	970
330		0.5	0.110	+0.001	0.109	1060
340		0.2	0.119	+0.001	0.118	1150
350		0.2	0.120	+0.001	0.119	1160
360		0.2	0.111	+0.001	0.110	1070
370		0.2	0.102	0.000	0.102	1000
380		0.2	0.089	0.000	0.089	870
390		0.2	0.075	0.000	0.075	730
400		0.05	0.062	0.000	0.062	610

TABLE LIII. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 75 PERCENT ETHYLENE GLYCOL-25 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/26/59	1.0	0.301	-0.018	0.319	3120
230		0.5	0.292	-0.018	0.310	3020
240		0.5	0.251	-0.026	0.277	2690
250		0.5	0.220	-0.018	0.238	2320
260		0.5	0.182	-0.006	0.188	1840
270		0.5	0.139	-0.003	0.142	1390
280		0.5	0.111	-0.002	0.113	1110
290		0.5	0.097	-0.002	0.099	970
300		0.5	0.098	-0.002	0.100	980
310		0.5	0.114	-0.001	0.115	1120
320		0.5	0.136	-0.001	0.137	1340
320		0.5	0.137	0.000	0.137	1340
330		0.5	0.157	0.000	0.157	1530
340		0.2	0.171	0.000	0.171	1670
350		0.2	0.174	0.000	0.174	1700
360		0.2	0.165	0.000	0.165	1610
370		0.2	0.150	0.000	0.150	1470
380		0.2	0.133	0.000	0.133	1300
390		0.2	0.114	0.000	0.114	1110
400		0.05	0.094	0.000	0.094	920

TABLE LIV. ABSORBANCY AND MOLAR ABSORBANCY INDEX FOR 1.026×10^{-4} MOLAR IRON (III) PERCHLORATE IN 90 PERCENT ETHYLENE GLYCOL–10 PERCENT WATER. (b = 0.998 cm.)

λ (mμ)	Date	Slit Width	A_s	Cell Correction	A'_s	a_M
220	2/22/59	1.2	0.086	-0.013	0.099	970
230		0.6	0.171	-0.024	0.195	1910
240		0.5	0.208	-0.017	0.225	2220
250		0.5	0.217	-0.005	0.222	2170
260		0.5	0.198	-0.002	0.200	1960
270		0.5	0.164	-0.002	0.166	1620
280		0.5	0.137	-0.002	0.139	1360
290		0.5	0.121	-0.002	0.123	1200
300		0.5	0.125	-0.002	0.127	1240
310		0.5	0.146	-0.002	0.148	1450
320		0.5	0.179	-0.002	0.181	1770
320		0.5	0.179	0.000	0.179	1750
330		0.5	0.212	0.000	0.212	2070
340		0.2	0.231	0.000	0.231	2260
350		0.2	0.240	0.000	0.240	2350
360		0.2	0.233	0.000	0.233	2280
370		0.2	0.212	0.000	0.212	2070
380		0.2	0.187	0.000	0.187	1830
390		0.2	0.160	0.000	0.160	1560
400		0.05	0.132	0.000	0.132	1290

DISCUSSION OF RESULTS

Cell Corrections

The silica cells used were matched within two percent transmittance, over the range studied, except at 220 millimicrons where they are matched to three percent according to manufacturers' specifications. To correct for this two or three percent difference and a slight difference in cell length, one cell was calibrated against the other.

For the solutions which were $1.03_4 \times 10^{-2}$ molar and 1.030×10^{-3} molar iron(III) perchlorate it was necessary to use a shorter cell length in order to obtain data in the region 200 to 320 millimicrons. This was accomplished by placing a silica cell spacer inside the one centimeter cells. It was found, while determining cell corrections, that the cell corrections were reproducible for a given solvent ratio, but that they varied with different solvents. For a comparison see the cell corrections for corresponding solutions with the same cell length (Tables I through XII).

It was thought that this might be explained in terms of an internal variation noticed in the cell spacers. This is probably not the case however, for a comparison of the values (Tables XIII through XVIII) obtained when the cell spacers were not used shows that a variation still occurs as the solvent ratio is changed.

There is no observable relationship in the variations. As a result the cell corrections applied to a solution were those obtained using the corresponding blank solution.

Kinetic Study

The solutions used in this study had been allowed to age for at least a week after dilution. This was done because of reported changes (1, 24, 26, 35, 42, 48) in properties with time. On the basis of the five days used for aging by Milburn and Vosburgh (42) and the fact that no visible precipitate had formed, it was assumed that the solutions were at equilibrium.

As mentioned previously, the first technique used in this study was to obtain that portion of the spectrum below 320 millimicrons for all the solutions and then obtain the portion above 320 millimicrons. In doing this a period of several days elapsed between the time the first and the last portions of a given spectrum was obtained. It was noted that the value obtained at 320 millimicrons, which overlaps the two portions of the spectrum, was not being reproduced. This fact raised a question as to whether or not the solutions were at equilibrium (Tables I through XVIII).

To check this, an additional period of approximately two weeks was allowed for aging and the solutions were checked again (Tables XIX through XXXVI). This time the entire spectrum of a given solution, in the range studied, was obtained at once. In comparing this data with that obtained from the first set of spectra, it was found that the entire curve had changed position. This indicated that an equilibrium had not been attained.

As a more complete check on this idea, another set of spectra (Tables XXXVII through LIV) was obtained approximately two weeks after

the second. In addition a kinetic study was made, since it was thought that the "aging" might be accelerated by increasing the temperature.

The kinetic study was made on fresh solutions of 1.034×10^{-2} molar iron(III) perchlorate in a 55 percent ethylene glycol-45 percent water solvent. The spectrum of this solution was obtained and one sample placed in an oven at 60 degrees centigrade while another was allowed to sit at room temperature, approximately 25 degrees centigrade.

A portion of the sample from the oven was put into a test tube and placed in the constant temperature bath for 15 to 20 minutes to allow it to attain a temperature of 25 degrees centigrade. The absorption spectrum was then recorded. This procedure was carried out at intervals for about four days. The sample which was to be used as a control was measured at intervals over the same period.

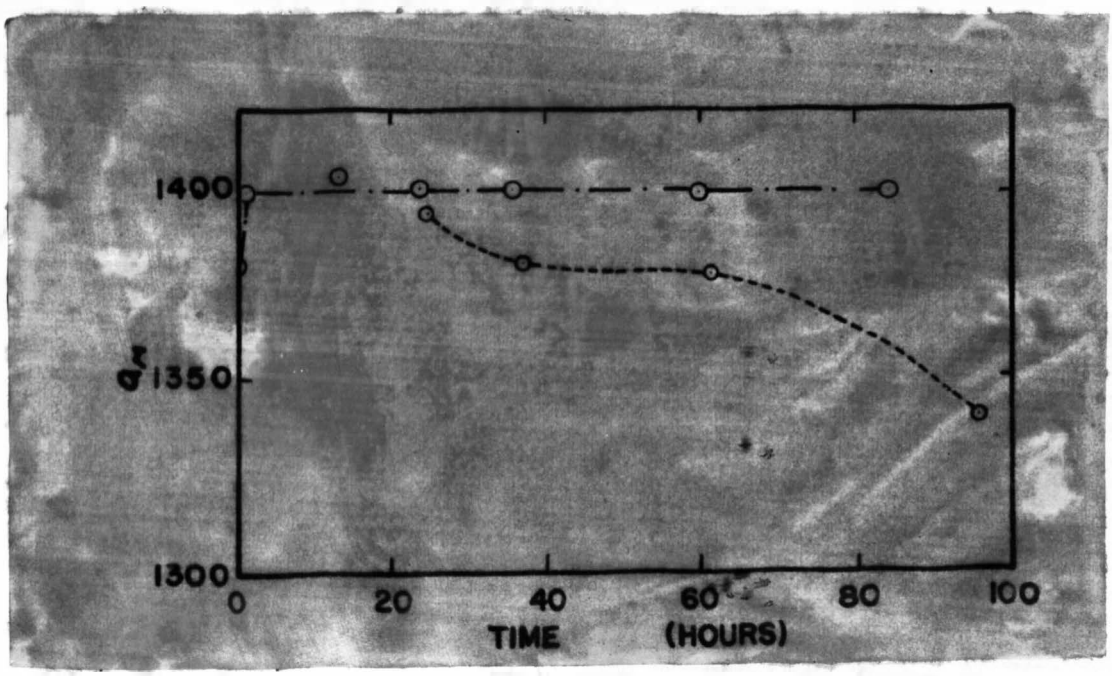

Figure 1. The Effect of Light on a 1.034×10^{-2} Molar Iron(III) Perchlorate Solution in the Solvent 75 Percent Ethylene Glycol-25 Percent Water

The results (Figure 1) indicate that the solution was not at equilibrium when first measured, but after one hour at 60 degrees centigrade the readings (solid line) were constant. More interesting were the values (dashed line) obtained for the sample which was allowed to remain at room temperature. The general decrease in absorbancy values can only be attributed to a photochemical reaction when compared to the values obtained from the sample kept in the oven.

Several authors have reported photoreduction of iron(III) ions which are involved in complex formation or are in the presence of a reducing medium (5, 6, 11, 20, 34, 49, 50, 54, 60).

Figures 2 and 3 show the relative change of the molar absorbancy index with time at the absorption maxima, in the long wave portion of the spectrum, for the solutions which are approximately 10^{-2} and 10^{-4} molar iron(III) perchlorate. The period between the successive values is about two weeks. A comparison of these two figures shows that the change is greater for the higher metal ion concentration.

The results for the solutions approximately 10^{-3} molar are intermediate to those plotted.

The conclusion was reached that there is a photochemical reduction of iron(III) ion in the presence of ethylene glycol with a decrease in absorbancy.

The Effect of Hydrogen Ion Concentration

Measurement of the hydrogen ion concentration of the solutions showed a variation in pH (Table LV) as the solvent was varied. The pH of a 8.43×10^{-2} molar solution of perchloric acid was determined to be

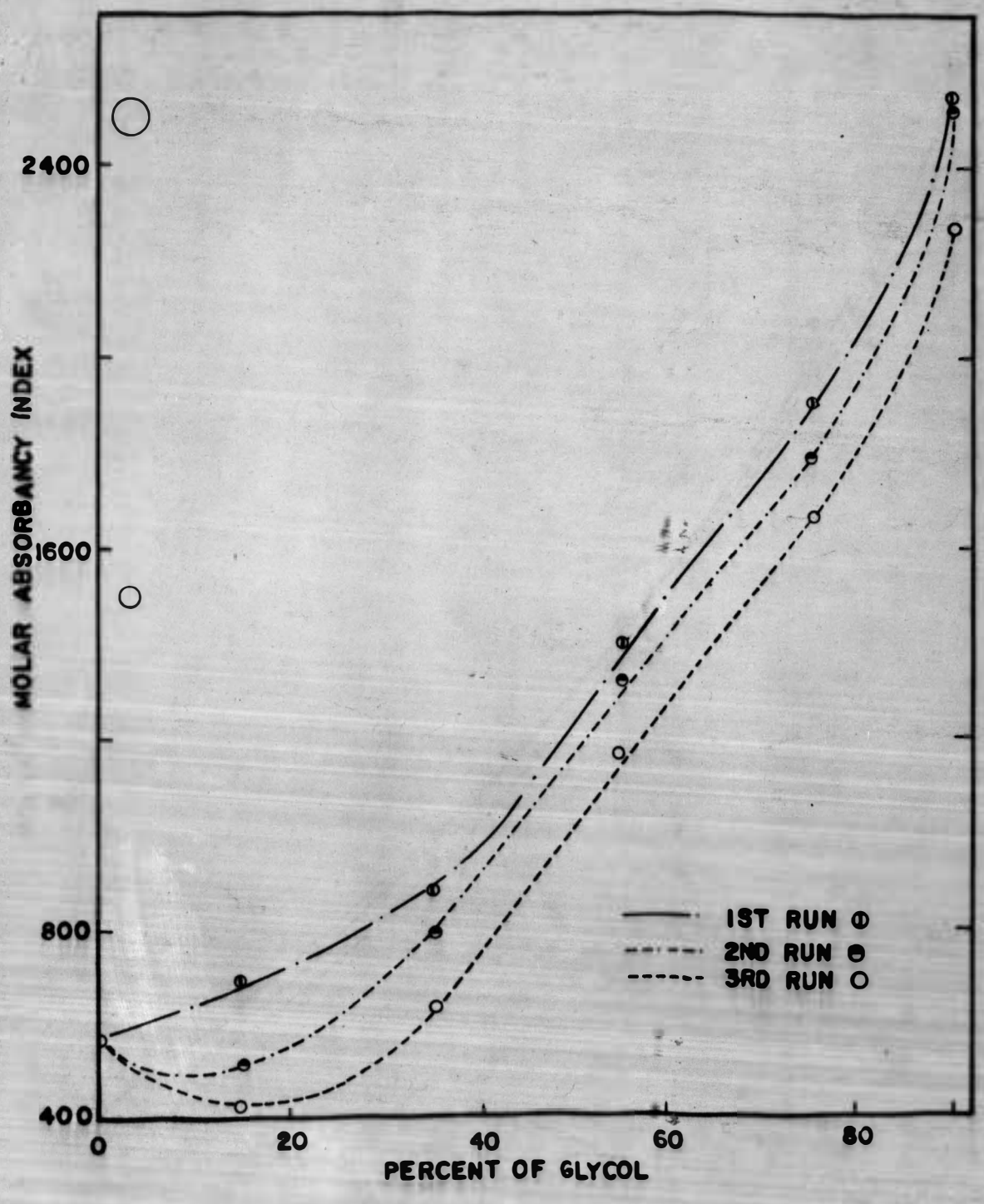

Figure 2. The Change of Molar Absorbancy Index with Time for 1.034×10^{-2} Molar Iron(III) Perchlorate Solutions

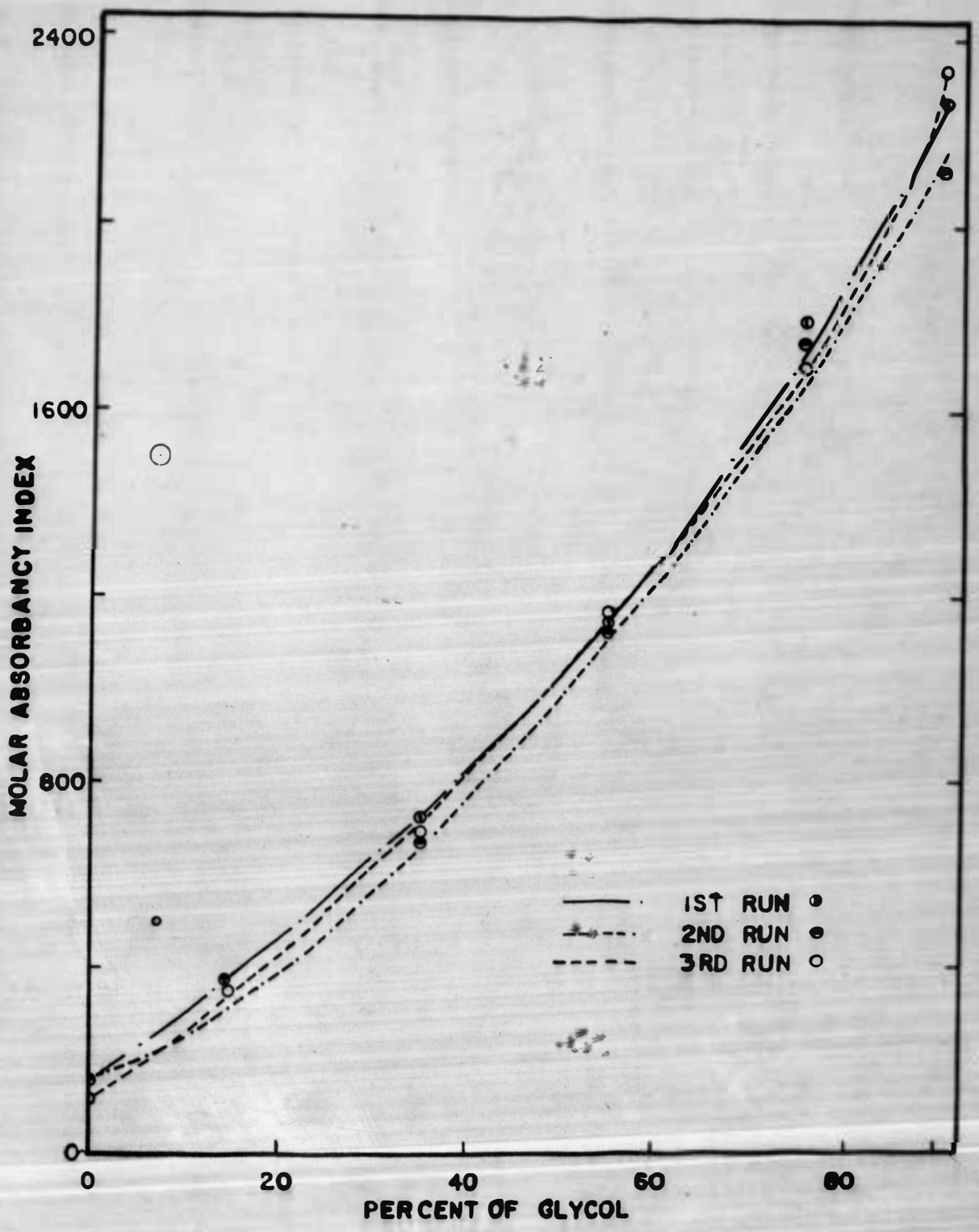

Figure 3. The Change of Molar Absorbancy Index with Time for 1.026×10^{-4} Molar Iron(III) Perchlorate Solutions

approximately 1.2 pH units. Comparing this to the pH values of the water solutions at the three different metal ion concentration it is observed that the three solutions vary somewhat from this value. The values indicate that there is appreciably more hydrolysis in the most concentrated solution.

TABLE LV. THE pH OF IRON(III) PERCHLORATE SOLUTIONS AT VARYING ETHYLENE-GLYCOL-WATER RATIOS (PERCHLORIC ACID = 8.43×10^{-2} M.)

Percent of Ethylene Glycol	I*	II*	III*
0	1.3	1.4	1.4
15	1.1	1.4	1.9
35	1.6	1.8	1.8
55	1.5	1.8	1.6
75	1.3	1.6	1.6
90	0.9	1.1	1.2

* I = 1.034×10^{-2} M. iron(III) Perchlorate
II = 1.030×10^{-3} M. iron(III) Perchlorate
III = 1.026×10^{-4} M. iron(III) Perchlorate

When ethylene glycol is added the pH changes. The values reported (Table LV) for the 10^{-2} and 10^{-3} molar solutions containing 15 percent ethylene glycol are probably in error. The readings when first taken were about 0.5 or 0.6 pH units higher, but the meter needle drifted to the recorded values. Later measurements on one of these solutions indicated that the higher value was probably correct. Assuming that these values should be higher the increase in pH could be explained by a replacement of hydroxyl ion in the first hydrolysis product by molecules of ethylene glycol.

With increasing amounts of ethylene glycol the general trend is an increase in hydrogen ion concentration. This could be explained by assuming that in the photoreduction of iron(III) ion to iron(II) ion the corresponding oxidation resulted in the formation of hydrogen ion.

This would be a logical conclusion in view of the results of Bates and Uri (5) and the fact that later measurements of the hydrogen ion concentration indicated that it is increasing with time.

The Bouguer-Beer Law

The Bouguer-Beer law is sometimes known as the Beer-Lambert law or simply Beer's law. It is commonly represented by

$$\frac{I}{I_o} = 10^{-a_s bc} = T_s,$$

where I_o = the intensity of the incident light, I = the intensity of the transmitted light, T_s = the transmittancy, a_s = the absorbancy index, b = the thickness of the absorbing solution, and c = the concentration of the absorbing species.

The Maxima in the Long Wave Region

A comparison (Figures 4, 5, 6) of the molar absorbancy indices, a_M, in the region of 340 millimicrons show a deviation from Beer's law. There are many things which can cause a deviation from this law, such as, non-monochromaticity of light, change in refractive index with concentration, and instrument error.

It is felt that although there may be contributions from other sources, the deviation in this case is in the main result of two related phenomena: an interaction of the solvent with the absorbing species,

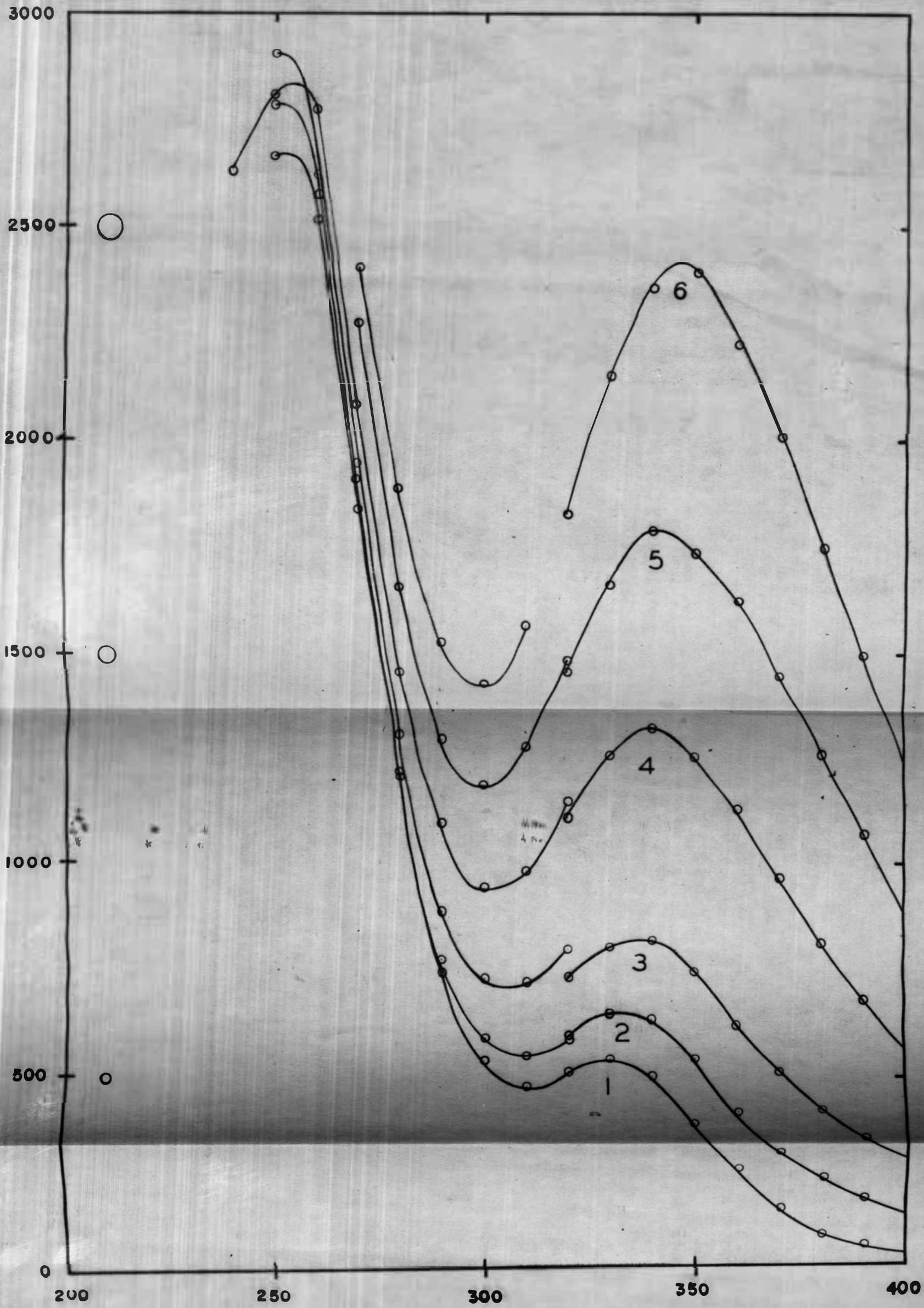

Figure 4. Absorption Curves for 1.034×10^{-2} Molar Iron(III) Perchlorate At Various Ratios of Ethylene Glycol-Water

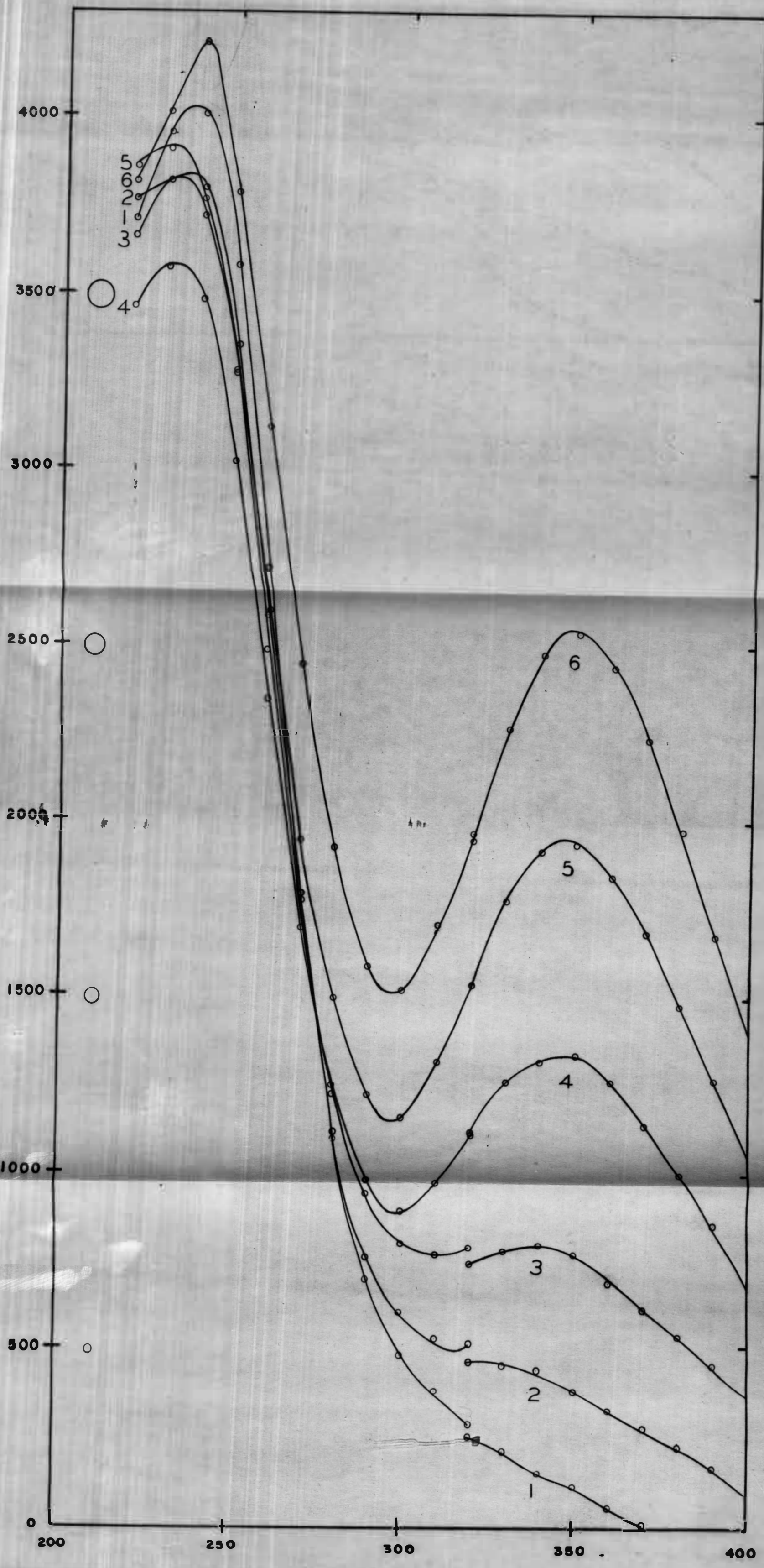

Figure 5. Absorption Curves for 1.030×10^{-3} Molar Iron(III) Perchlorate at Various Ratios of Ethylene Glycol-Water

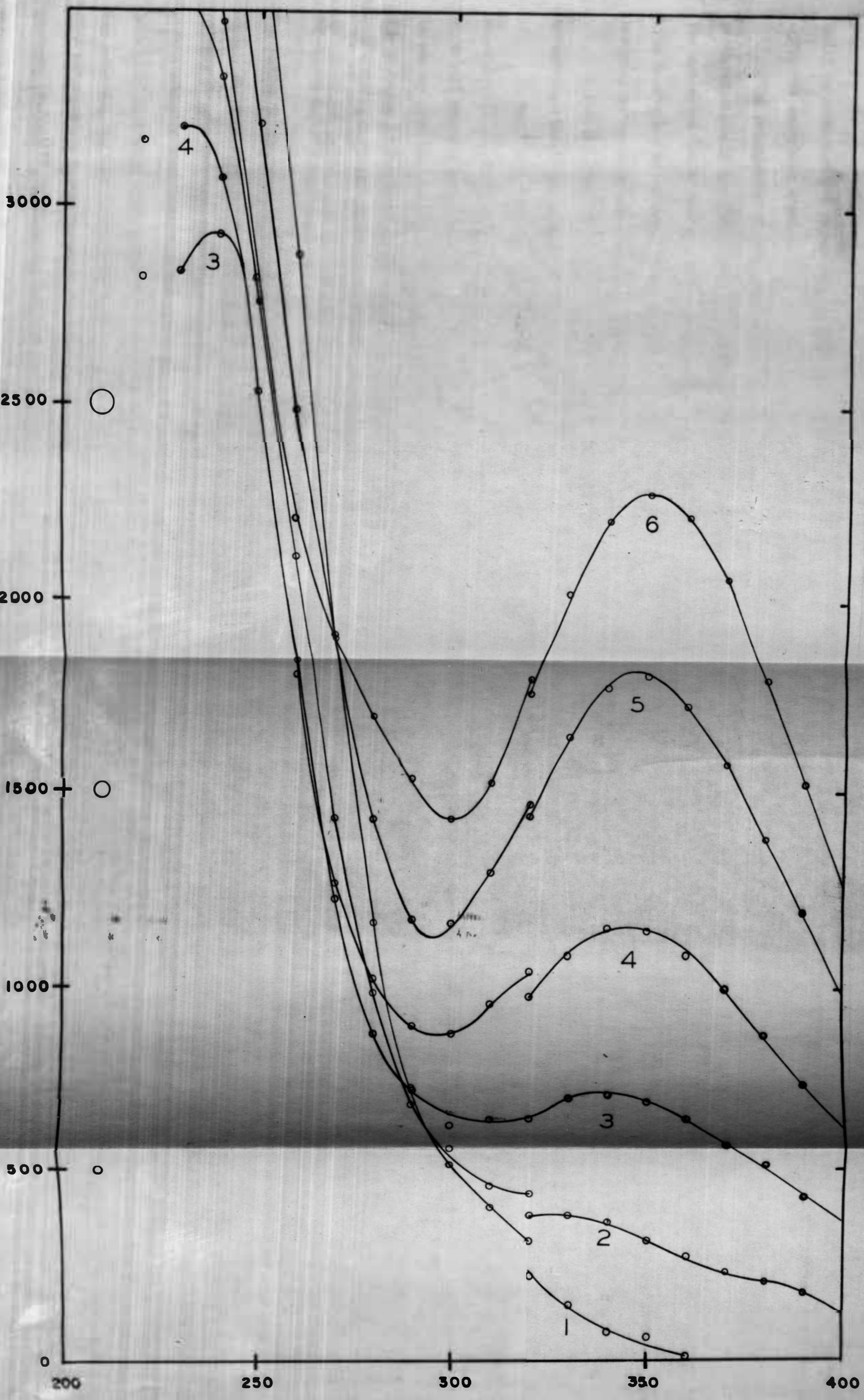

Figure 6. Absorption Curves for 1.026×10^{-4} Molar Iron(III) Perchlorate at Various Ratios of Ethylene Glycol-Water

which is concentration dependent, and/or an equilibrium involving different absorbing species.

The interaction of the solvent with iron(III) ion results in the photoreduction of iron(III) ion. The amount of reduction is dependent on the concentration of the iron(III) ion. This would result in a deviation from Beer's law since calculation of the molar absorbancy index involves dividing by the original concentration of the iron(III) ion.

A reverse reaction in the photoreduction mechanism would also effect the absorption spectra so as to give a deviation from Beer's Law.

It was found that the addition of perchloric acid to a 1.026×10^{-4} molar iron(III) perchlorate solution in the solvent 75 percent ethylene glycol-25 percent water eliminated the observed maximum. This would be in accord with the postulate that the photoreduction of iron(III) ion in the presence of ethylene glycol resulted in the formation of hydrogen ion, the hydrogen ion concentration effecting the equilibria of the absorbing species.

The Maxima in the Short Wave Region

It is interesting to note that in the region of 240 millimicrons Glikman et al. (20) have reported no change in the maximum located there as the ratio of their solvent, ethanol-water, was varied. Most authors have concluded that this maximum is due to hydrated iron(III) ions only. The exception to this is the conclusion of Rabinowitch and Stockmayer (51) that in aqueous solution there is a contribution from the first hydrolysis product, $\left[Fe(OH)\right]^{+2}$, in this region, and that its absorbancy index is greater than that of the hydrated iron(III) ion.

The curves (Figures 4, 5, 6) show that Beer's law is not obeyed in this region. The curves for the 1.030×10^{-3} and 1.026×10^{-4} molar iron(III) perchlorate solution show at first a general decrease in the molar absorbancy index as the percent of ethylene glycol increases.

In the case of the 1.030×10^{-4} molar iron(III) perchlorate solutions (Figure 6) there is a decrease in the molar absorbancy index for curves 1, 2 and 3, these corresponding to 100 percent water, 15 percent ethylene glycol and 35 percent ethylene glycol, respectively. For the remaining three curves, this trend is reversed.

The same type of trend is more apparent in the 1.026×10^{-3} molar iron(III) perchlorate solutions (Figure 5). Curves 1, 2, 3 and 4 show a decrease in molar absorbancy index, and then a change occurs which causes an increase in molar absorbancy index.

Assuming that an isobestic point is indicative of only two absorbing species or types of species in a solution, it is interesting to correlate this point with the decrease and increase of the molar absorbancy index at 240 millimicrons.

In Figure 5, an isobestic point exists at approximately 275 millimicrons. This point involves the same four solutions that show a decrease in absorbancy at 240 millimicrons. Curves 5 and 6 are not involved in this isobestic point, and they show an increase in molar absorbancy index at 240 millimicrons.

This would indicate that either a new species has been formed which absorbs in the 240 millimicron area or that the addition of more ethylene glycol has disturbed the equilibria in some way as to increase the concentration of hydrated iron(III) ion.

Milburn and Vosburgh (42) have reported that the type of species present in aqueous solution varies with the iron(III) ion concentration. In 10^{-2} molar solutions polynuclear species are present. The 10^{-4} molar solutions have mononuclear species, while the 10^{-3} molar solutions are intermediate. They vary the hydrogen ion concentration at all three levels of iron(III) ion concentration and obtain an isobestic point for the 10^{-4} molar solutions. This point is located at 273 millimicrons. They use this point as confirmatory evidence for mononuclear species.

In view of results of this study it is logical to assume that there is a fundamental difference in the species present at a given iron(III) ion concentration as the percentage of ethylene glycol is varied, and that different species are present at different iron concentrations.

A Glycol or Hydroxyl Complex

The absorption maxima occurring in the long wave portion of the spectrum are in the same region as are the absorption maxima of iron(III) ion hydrolysis products. This fact raises a question as to whether or not the different maxima observed were due to interaction of ethylene glycol and iron(III) ion.

Assuming that the ethylene glycol acted merely as a neutral phase which served only to change the amount of reactive solvent, water, then the iron(III) ion concentration would be in effect greater. This could conceivably produce the observed results.

The various possibilities were examined on the basis of three facts. First, for certain mixed solvent ratios, the addition of sodium

hydroxide did not precipitate iron(II) or iron(III) hydroxide until many times the equivalent amount had been added. A six milliliter sample of $1.03_4 \times 10^{-2}$ molar iron(III) perchlorate in 75 percent ethylene glycol-25 percent water was diluted to 30 milliliters with six molar sodium hydroxide without formation of a precipitate. This is in qualitative agreement with Traube (62). Second, Grün and Bockisch (22) reported that ethylene glycol was observed to replace water from the hydration sphere of heavy metals, each ethylene glycol molecule replacing two molecules of water. Third, the concentration of the absorbing species is pH dependent.

The third fact would seem to rule out the ethylene glycol complex. However, a series of complexes of a certain type could be formed, as postulated by Glikman et al. (20) which would absorb in the same region giving rise to a diffuse band. These could include a metal ion associated with the ligands OH^-, $(C_2H_4OH)_2$, H_2O, $C_2H_5O_2^-$, or combinations of these ligands. A ligand of the type $C_2H_5O_2^-$ could explain the fact that the absorbing species is pH dependent since dissociation of ethylene glycol to give this species would also give a hydrogen ion.

The results indicate that the absorption of iron(III) solutions in the long wave portion of the spectrum when ethylene glycol is present is due to a complex of iron(III) ion with ethylene glycol or products of solvolysis.

The Calculation of Stability Constants

Most of the present methods for calculating stability constants (52) from spectrophotometric data are all based on Beer's law. If the

solutions studied do not obey Beer's law, an empirical formula must be developed relating the variable or variables causing deviation and the absorbancy.

One possible method of determining stability constants when the solutions do not obey Beer's law is the use of an isobestic point if one is present. At this point the molar absorbancy indices for the two types of species are equal and, in effect, are obeying Beer's law at that particular wave length.

The data obtained in this study are not applicable to the calculation of stability constants. The presence of iron(II) ion as a result of photoreduction of iron(III) ion makes the iron(III) ion concentration unknown. In addition, the deviation from Beer's law makes it impossible to use available methods.

One possibility presented for determining a stability constant for the complex formed in these solutions is an isobestic point, for example the one observed in the 10^{-3} molar solutions at lower percentages of ethylene glycol. A possible study of this point at known pH values might give the data necessary for calculation of stability constants and formulas.

CONCLUSIONS

1. There is a photoreduction of iron(III) ion when it is associated with ethylene glycol.

2. The absorption maximum in the region of 340 millimicrons is due to a complex of iron(III) ion with ethylene glycol, with the solvolysis products of ethylene glycol, or combinations of the above ligands with hydroxyl radicals.

3. The system iron(III) perchlorate-ethylene glycol-water shows apparent deviations from the Bouguer-Beer law in the long wave portion, and in the short wave portion.

4. There is a fundamental difference in the species present as the iron ion concentrations and/or the solvent ratios are varied.

5. The presence of an isobestic point in the 10^{-3} molar iron(III) perchlorate solutions might allow the calculation of a stability constant with further study.

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